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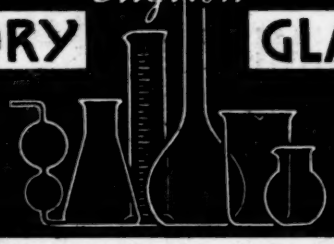

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less needles, m. p. 147—148° (Found : C, 66·8; H, 3·3. $C_{12}H_7N_2Cl$ requires C, 67·1; H, 3·3%), very slightly soluble in water, soluble in alcohol, moderately easily soluble in methyl alcohol, insoluble in light petroleum, soluble in dilute mineral acids but insoluble in dilute sodium hydroxide solution.

5 : 6 : 2′ : 3′-*Pyridoquinolinium Methyl Sulphate.*—5 : 6 : 2′ : 3′-Pyridoquinoline (*m*-phenanthroline) (0·9 g.) and methyl sulphate (0·46 c.c.) were refluxed in methyl alcohol (15—20 c.c.) for 1 hour and the methyl alcohol was then removed by distillation; a reddish-yellow crystalline mass remained which, recrystallised from methyl alcohol, yielded pale yellow, rectangular prisms, m. p. 192°, of 5 : 6 : 2′ : 3′-*pyridoquinolinium methyl sulphate* (Found : C, 53·4; H, 3·7. $C_{12}H_8N_2,HMeSO_4$ requires C, 53·4; H, 4·1%). This somewhat hygroscopic salt readily dissolved in water and when the solution was basified 5 : 6 : 2′ : 3′-pyridoquinoline was precipitated. This showed that the quaternary salt had not been formed.

1-*Methyl*-5 : 6 : 2′ : 3′-*pyridoquinolinium Methyl Sulphate* (N-*Methyl*-m-*phenanthrolinium Methyl Sulphate*).—Freshly distilled 5 : 6 : 2′ : 3′-pyridoquinoline (3·6 g.) and methyl sulphate (1·84 c.c.), dried over potassium carbonate, were warmed on the water-bath for 1 hour. When acetone was added to the reddish-brown liquid, the latter changed to a sticky solid, which became crystalline on repeated washing with acetone. This very hygroscopic material, dried in a desiccator over sulphuric acid, melted at about 145°. When a concentrated solution in alcohol was cooled, crystals separated which melted at about 130°. Part of the alcohol was removed from the mother-liquor, and acetone added; on cooling, a further crop of crystals was obtained, m. p. 162—164°, 168—169° after recrystallisation, and was evidently identical with the methylpyridoquinolinium methyl sulphate, m. p. 171°, mentioned in D.R.-P. 654,444.

Conversion of 2-*Keto*-1-*methyl*-1 : 2-*dihydro*-5 : 6 : 2′ : 3′-*pyridoquinoline into* 2-*Chloro*-5 : 6 : 2′ : 3′-*pyridoquinoline* (cf. D.R.-P. 654,444).—2-Keto-1-methyl-1 : 2-dihydro-5 : 6 : 2′ : 3′-pyridoquinoline (m. p. 194°) (0·5 g.), prepared from slightly impure 1-methyl-5 : 6 : 2′ : 3′-pyridoquinolinium methyl sulphate by oxidation with alkali ferricyanide, was refluxed with phosphorus oxychloride (1 c.c.) and pentachloride (1 g.) at 150—160° for 10 hours. The homogeneous solution was cooled, treated with water, filtered, and basified with sodium hydroxide solution; the brownish precipitate which separated, after recrystallisation from aqueous alcohol, had m. p. 148—149°, not depressed by 2-chloro-5 : 6 : 2′ : 3′-pyridoquinoline (m. p. 147—148°) prepared from 2-hydroxy-5 : 6 : 2′ : 3′-pyridoquinoline, but considerably depressed by 2-chloro-7 : 8 : 2′ : 3′-pyridoquinoline.

The following amines were obtained by refluxing the appropriate chloropyridoquinolines and bases in the presence of a trace of copper bronze for several hours. The excess of amine was removed in a vacuum, the product treated with dilute sodium hydroxide solution and extracted with ether, and the ether removed from the dried extract by distillation. The base obtained sometimes crystallised; otherwise it was converted into the hydrobromide by treatment with fuming alcoholic hydrogen bromide or into the picrate by addition of an ethereal or alcoholic solution of picric acid to a solution of the base in the same solvent. None of the first four bases or their salts showed fluorescence in solution. The last four bases showed a weak green fluorescence in ethereal solution but none in dilute mineral acid. All the bases, except the two described as crystalline, were recovered as oils from their picrates.

4-(β-Diethylaminoethylamino)-2-methyl-5 : 6 : 2′ : 3′-pyridoquinoline, from 4-chloro-2-methyl-5 : 6 : 2′ : 3′-pyridoquinoline (0·5 g.) and β-diethylaminoethylamine (1 c.c.), refluxed at 150° for 6 hours. The *dipicrate*, recrystallised from methyl ethyl ketone, formed small, bright yellow plates, m. p. 237°, in almost theoretical yield (Found : C, 48·6; H, 3·7. $C_{19}H_{24}N_4,2C_6H_3O_7N_3$ requires C, 48·6; H, 3·9%); it was very slightly soluble in water, methyl alcohol, alcohol and benzene, but somewhat more soluble in acetone.

4-(δ-Diethylamino-α-methylbutylamino)-2-methyl-5 : 6 : 2′ : 3′-pyridoquinoline, from 4-chloro-2-methyl-5 : 6 : 2′ : 3′-pyridoquinoline (0·5 g.) and δ-diethylamino-α-methylbutylamine (1 c.c.), refluxed for 8 hours at 200°. The *dipicrate*, recrystallised from methyl ethyl ketone, formed brownish-yellow plates, m. p. 195° (yield, almost theoretical) (Found : C, 50·4; H, 4·4. $C_{22}H_{30}N_4,2C_6H_3O_7N_3$ requires C, 50·5; H, 4·5%), very slightly soluble in water, methyl alcohol, alcohol and benzene and to a small extent in hot acetone.

4-(β-*Diethylaminoethylamino*)-2-*methyl*-7 : 8 : 2′ : 3′-*pyridoquinoline*, from 4-chloro-2-methyl-7 : 8 : 2′ : 3′-pyridoquinoline (1·0 g.) and β-diethylaminoethylamine (2 c.c.), refluxed at 150° for 8 hours, crystallised from light petroleum in pale yellow plates (1 g.), m. p. 115—116° (Found : C, 73·1; H, 8·0. $C_{19}H_{24}N_4$ requires C, 74·0; H, 7·8%), very soluble in alcohol, acetone, benzene and ether, insoluble in water and dilute sodium hydroxide solution, but readily soluble in dilute mineral acid. It readily absorbed carbon dioxide from the atmosphere and consequently was difficult to purify. The *trihydrobromide* crystallised from alcohol in colourless needles, m. p. 284—285° (Found : C, 41·8; H, 4·6. $C_{19}H_{24}N_4,3HBr$ requires C, 41·4; H, 3·9%). This salt is very hygroscopic and is readily soluble in water, but insoluble in benzene, ligroin and acetone.

4-(δ-Diethylamino-α-methylbutylamino)-2-methyl-7 : 8 : 2′ : 3′-pyridoquinoline, from 4-chloro-2-methyl-7 : 8 : 2′ : 3′-pyridoquinoline (1·0 g.) and δ-diethylamino-α-methylbutylamine (2 c.c.), refluxed for 8 hours at 200°, was obtained as an oil which yielded solid derivatives with picric acid, methylenedisalicylic acid and flavianic acid. The last two were amorphous and very sparingly soluble in most organic solvents. The bright yellow picrate was best purified by conversion into the base and precipitation with picric acid in ethereal solution. Analysis suggested that it was the *tripicrate* (Found : C, 46·9; H, 3·3. $C_{22}H_{30}N_4,3C_6H_3O_7N_3$ requires C, 46·3; H, 3·9%). It shrank at 85° and melted at 130° and was soluble in acetone but insoluble in most other common solvents.

2-(β-*Diethylaminoethylamino*)-4-*methyl*-7 : 8 : 2′ : 3′-*pyridoquinoline*, from 2-chloro-4-methyl-7 : 8 : 2′ : 3′-pyridoquinoline (0·7 g.) and β-diethylaminoethylamine (1·4 c.c.), refluxed at 150° for 6 hours, crystallised from

light petroleum in clusters of pale yellow needles (0·7 g.), m. p. 113—114° (Found: C, 74·2; H, 8·3. $C_{19}H_{24}N_4$ requires C, 74·0; H, 7·8%), very soluble in alcohol, acetone and methyl alcohol, soluble in benzene, moderately easily soluble in light petroleum, insoluble in water and dilute sodium hydroxide solution but easily soluble in cold dilute mineral acid. It readily absorbed carbon dioxide from the atmosphere. The *dihydrobromide* crystallised from alcohol in long, pale yellow needles, m. p. 281—283° (decomp.) (Found: C, 47·8; H, 5·5. $C_{19}H_{24}N_4,2HBr$ requires C, 48·5; H, 5·5%), soluble in water and methyl alcohol but insoluble in benzene, ligroin and acetone.

2-(δ-Diethylamino-α-methylbutylamino)-4-methyl-7 : 8 : 2′ : 3′-pyridoquinoline, from 2-chloro-4-methyl-7 : 8 : 2′ : 3′-pyridoquinoline (0·7 g.) and δ-diethylamino-α-methylbutylamine (1·4 c.c.), refluxed at 200° for 8 hours. The *monopicrate*, recrystallised from methyl ethyl ketone, melted at 260° after decomposition at about 230° (Found: C, 57·6; H, 5·3. $C_{22}H_{30}N_4,C_6H_3O_7N_3$ requires C, 58·0; H, 5·7%); it was very slightly soluble in water, alcohol and benzene but somewhat more soluble in hot acetone.

2-(β-Diethylaminoethylamino)-5 : 6 : 2′ : 3′-pyridoquinoline, from 2-chloro-5 : 6 : 2′ : 3′-pyridoquinoline (0·5 g.) and β-diethylaminoethylamine (1 c.c.), refluxed at 150° for 5 hours. The *dipicrate* crystallised from methyl ethyl ketone in small, yellow, rectangular plates, m. p. 223—224° (Found: C, 47·9; H, 3·8. $C_{18}H_{22}N_4,2C_6H_3O_7N_3$ requires C, 47·9; H, 3·7%), very slightly soluble in water, methyl alcohol, alcohol and benzene, but more soluble in acetone, from which it crystallised.

2-(δ-Diethylamino-α-methylbutylamino)-5 : 6 : 2′ : 3′-pyridoquinoline, from 2-chloro-5 : 6 : 2′ : 3′-pyridoquinoline (0·8 g.) and δ-diethylamino-α-methylbutylamine (1·6 c.c.), refluxed at 200° for 8 hours. The *dipicrate* crystallised from methyl ethyl ketone in small yellow prisms (1·6 g.), m. p. 195° (Found: C, 50·0; H, 4·1. $C_{21}H_{28}N_4,2C_6H_3O_7N_3$ requires C, 49·9; H, 4·3%), slightly soluble in alcohol, methyl alcohol, water, and benzene and somewhat more soluble in acetone.

We thank the Medical Research Council for a grant to one of us (W. W.) which enabled this work to be carried out.

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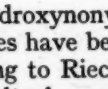
39. *Peroxides derived from η-Aldehydo-octoic Acid and Nonaldehyde: Bis-α-hydroxy-ω-carboxyoctyl Peroxide and Bis-α-hydroxynonyl Peroxide.*

By GEORGE KING.

Bis-α-hydroxy-ω-carboxyoctyl peroxide (II) and bis-α-hydroxynonyl peroxide (III) have been synthesised from η-aldehydo-octoic acid and nonaldehyde respectively. Although these peroxides are well-defined crystalline substances, the latter is particularly unstable, even in the solid form, and both tend to dissociate in solution to some extent into the free aldehydes and hydrogen peroxide. Their general reactions and peroxidising properties have been studied.

A PEROXIDE derived from η-aldehydo-octoic acid (azelaic semialdehyde) was first reported by Harries (*Ber.*, 1909, **42**, 455), who obtained it as one of the hydrolytic products of oleic acid ozonide, and assigned to it the structure (I). It was subsequently shown by Rieche and Sauthoff (*Sitzungsber. physik.-med. Soz. Erlangen*, 1929/30, **61**, 369) to belong to the class of bis-α-hydroxyalkyl peroxides, and to have the structure (II).



(I.)

$HO_2C\cdot[CH_2]_7\cdot CH(OH)\cdot O\cdot O\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$ (II.)

(III.) $CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot O\cdot O\cdot CH(OH)\cdot[CH_2]_7\cdot CH_3$

Bis-α-hydroxynonyl peroxide (III) affords another example of this type of compound, whose general properties have been described by Rieche ("Alkylperoxyde und Ozonide," 1931; *Ber.*, 1931, **64**, 2328). According to Rieche, both these peroxides occur among the products of cleavage of oleic acid ozonide as a result of secondary reactions involving the equilibrium

$$R\cdot CH(OH)\cdot O\cdot OH + R\cdot CHO \rightleftharpoons R\cdot CH(OH)\cdot O\cdot O\cdot CH(OH)\cdot R$$

rather than by the direct union of hydrogen peroxide and aldehydes arising during the decomposition. Although peroxides of type (III) can usually be synthesised readily from hydrogen peroxide and the corresponding aldehydes (Rieche, *loc. cit.*; Wieland and Wingler, *Annalen*, 1923, **431**, 301), Rieche was unable to obtain (II) in a similar manner from azelaic semialdehyde, doubtless because the latter itself had not at that time been isolated in even a reasonably pure state (King, J., 1938, 1826).

The author has found that η-aldehydo-octoic acid reacts smoothly and normally with hydrogen peroxide, affording bis-α-hydroxy-ω-carboxyoctyl peroxide in good yield, and advantage has been taken

of this to investigate its properties, as well as those of the corresponding peroxide derived from nonaldehyde. Both peroxides are well-defined crystalline substances, the former being distinctly the more stable, but experimental evidence suggests that in most media they undergo reversible dissociation into the free aldehydes and hydrogen peroxide, dissociation being promoted by rise of temperature, thus:

$$R{\cdot}CH(OH){\cdot}O{\cdot}O{\cdot}CH(OH){\cdot}R \rightleftharpoons 2R{\cdot}CHO + H_2O_2$$

Experimental.

Bis-α-hydroxy-ω-carboxyoctyl Peroxide (II).—η-Aldehydo-octoic acid (2·7 g., m. p. 38·5°), prepared from 9 : 10-dihydroxystearic acid (King, *loc. cit.*, p. 1827), in glacial acetic acid (20 ml.) was treated with hydrogen peroxide (1·0 ml. of 90—100 vol.) at room temperature; after 48 hours an equal bulk of water was added, and the whole cooled in ice-water. The product was collected, washed with 50% acetic acid and water (yield, 2·2 g., m. p. 112°), and recrystallised from acetone and alcohol, bis-α-hydroxy-ω-carboxyoctyl peroxide separating in small, somewhat elongated, hexagonal plates, m. p. 112·5° (decomp.) (Harries, *loc. cit.*, gave m. p. *ca.* 98°) [Found: C, 57·2; H, 9·0; equiv., 189; *M* (in dioxan), 343, 441. Calc. for $C_{18}H_{34}O_8$: C, 57·3; H, 9·0%; equiv. (dibasic), 189; *M*, 378]. The m. p. fell to 106° after the peroxide had been kept for 5 months over sulphuric acid in a desiccator.

The peroxide was very sparingly soluble in light petroleum, chloroform, and benzene, and sparingly in ether, acetone, and alcohol in the cold. It dissolved appreciably in boiling water, but with some decomposition. The peroxide gave colours with Schiff's reagent and with titanium sulphate solution only after being boiled for a few minutes with water and then cooled, suggesting dissociation into η-aldehydo-octoic acid and hydrogen peroxide. It liberated iodine rapidly from a warm solution of potassium iodide, but very slowly in the cold, and reduced Fehling's solution appreciably on boiling.

Action of Water and Aqueous Sodium Hydroxide on Bis-α-hydroxy-ω-carboxyoctyl Peroxide.—(*a*) The peroxide (0·5 g.), after being refluxed with water (25 ml.) for 8—9 hours, gave negative tests with titanium sulphate and potassium iodide: the cooled solution, treated with *p*-nitrophenylhydrazine in dilute acetic acid, deposited the *p*-nitrophenylhydrazone of η-aldehydo-octoic acid (0·42 g.; *ca.* 50%), which crystallised from alcohol and acetone in short orange rods or prisms, m. p. and mixed m. p. 144°. (A comparable solution of hydrogen peroxide required boiling for 7 hours to destroy all peroxide reactions.)

(*b*) A solution of the peroxide in cold 2N-sodium hydroxide gave an immediate yellow colour with titanium sulphate solution. On warming, some evolution of oxygen occurred and the solution then no longer gave peroxide reactions. After several minutes' boiling, acidification with 2N-sulphuric acid, and extraction with ether, a pale yellow, viscous oil was obtained, apparently identical in properties with the polymerised product resulting from the action of alkali on the semialdehyde itself (King, *loc. cit.*, p. 1828).

Further Properties of the Peroxide.—With semicarbazide hydrochloride and sodium acetate in warm aqueous alcohol, bis-α-hydroxy-ω-carboxyoctyl peroxide afforded the semicarbazone of η-aldehydo-octoic acid, m. p. and mixed m. p. 166·5° (Found: C, 52·3; H, 8·6; N, 18·0; equiv., 229. Calc. for $C_{10}H_{19}O_3N_3$: C, 52·4; H, 8·3; N, 18·3%; equiv., 229). Presumably, hydrogen peroxide was eliminated during this condensation, since the aqueous-alcoholic mother-liquor liberated iodine freely from potassium iodide.

Similarly, with Brady's reagent in warm 90% alcohol, the 2 : 4-dinitrophenylhydrazone of the semialdehyde readily separated, m. p. 120·5° after repeated crystallisation from alcohol, not depressed by an authentic specimen.

Further evidence of the ease with which the peroxide dissociates into the semialdehyde and hydrogen peroxide in various solvents was afforded by the immediate yellow colour obtained on adding titanium sulphate solution to a cold saturated solution in dioxan, a strong positive Schiff's reaction in the same solvent, and the rapid consumption of permanganate, with effervescence, in the presence of sulphuric acid. Similar results were obtained in cold alcoholic solution, and it was noteworthy that the peroxide dissolved more freely in alcohol containing dilute sulphuric acid than in alcohol alone.

Estimation of "Active Oxygen" by Lea's Method.—Bis-α-hydroxy-ω-carboxyoctyl peroxide (0·0341 g.) was treated in a Pyrex tube with potassium iodide (1·0 g.) and glacial acetic acid–chloroform (20 ml. of 2 : 1 by vol.), with the precautions described by Lea (D.S.I.R. Food Investigation Special Report No. 46, "Rancidity in Edible Fats," 1938, p. 107). After heating, pouring into water (30 ml.), and rinsing out, the liberated iodine required 16·35 ml. of N/100-sodium thiosulphate, allowance having been made for a blank (Calc.: 18·05 ml., assuming 1 atom of active O per mol.). The percentage of active oxygen found was therefore 3·84 (*i.e.*, 90·8% of the theoretical).

Oxidation of η-Aldehydo-octoic Acid by Labile Peroxides in Ether.—The occurrence of bis-α-hydroxy-ω-carboxyoctyl peroxide among the products of oxidation of the 9 : 10-dihydroxystearic acids with periodic acid has been observed by the author on several occasions. Its formation was ultimately traced to the oxidation of η-aldehydo-octoic acid by "labile peroxides" in the rather large bulk of ether used for extraction. These peroxides are readily detected by the yellow colour imparted to a few drops of titanium sulphate solution when shaken with several ml. of the ether, and can be removed by fractionation of the ether through a long column, the peroxides being less volatile. According to H. King (J., 1929, 738), old specimens of ether may contain the equivalent of 2—10 g. of hydrogen peroxide per l., mainly in the form of hydroxyethyl hydrogen peroxide, $CH_3{\cdot}CH(OH){\cdot}O{\cdot}OH$.

In one experiment, dihydroxystearic acid (3·11 g.), m. p. 132°, was oxidised with periodic acid in the manner previously described by the author (*loc. cit.*), and the products were extracted with ether (330 ml.) containing labile peroxides equivalent to 0·26 g. of hydrogen peroxide (estimated by the method of H. King, *loc. cit.*). After distillation of the solvent and removal of nonaldehyde by steam-distillation, the remaining aqueous liquid (*ca.* 100 ml.) was cooled, depositing crude bis-α-hydroxy-ω-carboxyoctyl peroxide (1·36 g., m. p. 99—101°). After being washed with ether and crystallised successively from alcohol and acetone, this melted at 112°, undepressed by an authentic specimen. The aqueous mother-liquor contained η-aldehydo-octoic acid (0·24 g.), recovered in the form of its 2 : 4-dinitrophenylhydrazone, m. p. 122°.

Bis-α-hydroxynonyl Peroxide (III).—Hydrogen peroxide (1·7 ml. of " 90—100 " vol.) was added to nonaldehyde (3·8 g.), prepared from dihydroxystearic acid (King, *loc. cit.*), in glacial acetic acid (25 ml.). Crystals began to separate almost immediately. After 24 hours at room temperature, an equal bulk of water was added, and the whole cooled in ice. The product (3·1 g., m. p. 73°) was crystallised twice from absolute alcohol, giving pure bis-α-hydroxynonyl peroxide in colourless, elongated, hexagonal plates, m. p. 78° (Harries and Franck, *Annalen*, 1910, **374**, 365, gave m. p. 72°) [Found: C, 67·9; H, 12·1; *M* (in dioxan), 306. Calc. for $C_{18}H_{38}O_4$: C, 67·9; H, 12·0%; *M*, 318]. This was very sparingly soluble in water and cold light petroleum, somewhat sparingly in alcohol, but readily in ether at room temperature. The peroxide was unstable even in the solid form, had a distinct odour of nonaldehyde, and lost all its peroxidising properties when kept over sulphuric acid in a desiccator for 14 days, becoming at the same time semi-liquid. Shaken with water and titanium sulphate solution, it gave no appreciable colour for some minutes, but a deep yellow colour developed at once on warming. Similarly, iodine was liberated slowly from aqueous potassium iodide in the cold, but rapidly on warming. A cold aqueous suspension slowly gave a magenta colour with Schiff's reagent. When boiled with water, the peroxide decomposed rapidly into nonaldehyde and hydrogen peroxide. Heated above its m. p., especially at 120—150°, it decomposed with effervescence, leaving a mixture of nonaldehyde and nonoic acid.

Estimation of " Active Oxygen " in Bis-α-hydroxynonyl Peroxide.—By Lea's method, 0·0348 g. of the peroxide liberated iodine equivalent to 21·5 ml. of N/100-sodium thiosulphate (Calc.: 21·85 ml.). The percentage of active oxygen found was therefore 4·94 (Calc., assuming one atom of active O per mol., 5·03%), *i.e.*, 98·2% of the theoretical.

Distillation of Bis-α-hydroxynonyl Peroxide with Aqueous Sulphuric Acid (cf. H. King, *loc. cit.*, p. 745).—The peroxide (0·40 g.) was distilled with 2N-sulphuric acid (25 ml.) and water (35 ml.) from a long-necked distilling flask for 20 mins., at the end of which time no further nonaldehyde came over. The clear residual liquid, after being cooled, required 22·7 ml. of N/10-potassium permanganate (Calc.: 25·16 ml., assuming complete decomposition of the peroxide into 2 mols. of nonaldehyde and 1 mol. of hydrogen peroxide), *i.e.*, the hydrogen peroxide obtained represented 90·2% of the theoretical. The aqueous distillate, containing nonaldehyde in suspension, was shaken with Brady's reagent (1 g. of 2 : 4-dinitrophenylhydrazine in 250 ml. of 2N-hydrochloric acid), giving nonaldehyde 2 : 4-dinitrophenylhydrazone (0·758 g., m. p. 104—105·5°. Calc.: 0·810 g.). This crystallised from alcohol in broad yellow needles, m. p. and mixed m. p. 106·5°.

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40. *The Crotonic Acid Series. Part II. Nitrogen Derivatives of α-Phenylcrotonic Acid.*

By M. A. Phillips.

The study of the nitrogen derivatives of crotonic acids commenced by Newbery (J., 1925, **127**, 295) and continued by the author (J., 1926, 2979) has been extended to the carbamides and the amide of α-phenylcrotonic (β-methylatropic) acid. Attention is called to the exceedingly reactive nature of the bromine atom in derivatives of α-bromo-α-phenylbutyric acid and to the extreme ease of hydrolysis of the unsaturated carbamides and of the unsaturated amide. In this respect these nitrogen derivatives of α-phenylcrotonic acid resemble the corresponding derivatives of crotonic acid and contrast with those of α-ethylcrotonic acid. In connection with this work, *α-bromophenylbutyrylcarbamide* and NN'-*bis*-(*α-phenylbutyryl*)*carbamide* were prepared.

It has been shown by Newbery (J., 1925, **127**, 295) that the action of caustic alkali on α-bromo-α-ethylbutyrylcarbamide (carbromal B.P.) gives mainly labile α-ethylcrotonylcarbamide, the bromine atom being removed as hydrogen bromide with some ease. The unsaturated carbamide and its stable isomeride are both hydrolysed with caustic alkali to give the corresponding forms of α-ethylcrotonamide, both of which were found to be surprisingly stable towards further treatment with sodium hydroxide. This

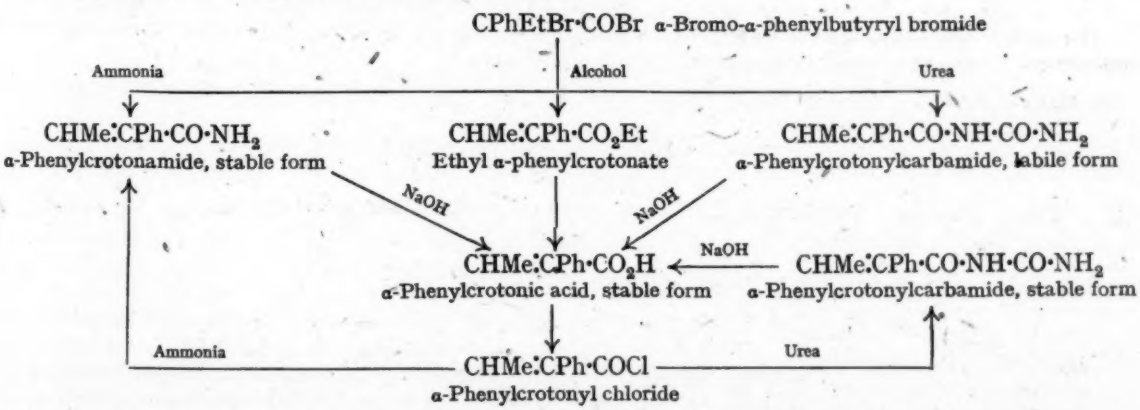
author also showed that the stable form of the amide was more readily hydrolysed by treatment with caustic alkali than was the labile form.

In Part I (Phillips, J., 1926, 2979) the investigation was extended to the study of the amides and carbamides of crotonic acid itself. It was shown that, as in the case of the higher homologues, the action of caustic alkali on α-bromobutyrylcarbamide gave labile crotonylcarbamide, and the isomeric unsaturated carbamide was formed from crotonyl chloride and urea. Further action even of limited amounts of sodium hydroxide solution on both these carbamides gave, not amide, but the corresponding form of crotonic acid. In consequence only the stable form of crotonamide was obtained. This was formed by the action of ammonia on crotonyl chloride, and was found to be hydrolysed by caustic alkali with extreme ease, the absence of amide in the action of alkali on the two forms of the carbamide thus being explained.

It has now been shown that similar principles apply to the nitrogen derivatives of α-phenylcrotonic acid. α-Bromo-α-phenylbutyrylcarbamide could not, however, be obtained from *α-bromo-α-phenylbutyryl bromide* and urea on account of the extreme ease with which the bromine atom is removed. This ease of removal of bromine as hydrogen bromide is very marked in this series of compounds; for example, the action of alcohol on the bromo-bromide gives mainly α-phenylcrotonic ester, and ammonia even under mild conditions gives α-phenylcrotonamide. The action of urea was shown to give one form of *α-phenylcrotonylcarbamide*. The other (lower-melting) form of the carbamide, designated the stable form by analogy with the corresponding form of α-ethylcrotonylcarbamide obtained by Newbery (*loc. cit.*), was obtained from *α-phenylcrotonyl chloride* and urea. Both forms of the carbamide are reduced to give α-phenylbutyrylcarbamide. On attempting to obtain the two forms of the amide by treatment of the isomeric carbamides with sodium hydroxide, it was found that both gave, under very mild conditions, excellent yields of the same, evidently the stable, form of α-phenylcrotonic acid identical with that prepared by Oglioloro (*Gazzetta*, 1885, **15**, 514) from paraldehyde, sodium phenylacetate and sodium acetate. α-Phenylcrotonamide, presumably the stable form, prepared from the acid chloride and ammonia gave an almost quantitative yield of α-phenylcrotonic acid on relatively mild treatment with caustic alkali.

The above series of derivatives of α-phenylcrotonic acid evidently resemble the simple crotonic acid series in their lability towards caustic alkali and stand in marked contrast to the α-ethylcrotonic acid derivatives described by Newbery (*loc. cit.*). This unexpected result can only be related to the positive nature of the phenyl radical. The ease with which the bromine atom is eliminated in the α-bromo-α-phenylbutyric acid series as compared with the relative stability in both the α-bromobutyryl and the α-bromo-α-ethylbutyryl series may be a further example of this.

The reactions described above are illustrated below:



Since the object of this work was the synthesis of α-bromo-α-phenylbutyrylcarbamide for comparison with α-bromo-α-ethylbutyrylcarbamide as an hypnotic agent, the bromination of α-phenylbutyrylcarbamide was attempted, but the bromine atom entered the benzene nucleus. This was shown by hydrolysis of the *α-bromophenylbutyrylcarbamide* formed, an α-bromophenylbutyric acid being obtained. The orientation of the bromine atom within the benzene nucleus has not been determined, but the compound is probably an *o*- or *p*-bromophenyl derivative. α-Phenylbutyrylcarbamide was obtained from *α-phenylbutyryl chloride* and urea at low temperatures; at higher temperatures NN'-*bis*-(*α-phenylbutyryl*)-*carbamide* is formed.

Tests on mice indicated that α-bromophenylbutyrylcarbamide has about one half the hypnotic activity of and is considerably more toxic than α-bromo-α-ethylbutyrylcarbamide.

Experimental.

α-Bromo-α-phenylbutyryl Bromide.—Dry bromine (144 g.) was added at 50° to α-phenylbutyryl chloride (Rising and Schwartz, *J. Amer. Chem. Soc.*, 1932, **54**, 2024) (157 g.), and the mixture refluxed until the bromine had been absorbed (2½ hours). After aspiration to remove dissolved hydrogen chloride, the residue was fractionated under reduced pressure. The *bromide* (195 g., 74% of the theoretical amount) was a colourless oil, b. p. 150—154°/22 mm. (Found: Br, 51·9. $C_{10}H_{10}OBr_2$ requires Br, 52·3%).

Action of Alcohol on α-Bromo-α-phenylbutyryl Bromide.—The acid bromide (50 g.) was added slowly at 60° to absolute alcohol (150 c.c.), the temperature being controlled by the rate of addition. After refluxing for 30 minutes and removal of the excess of alcohol, the residue was fractionated at 10 mm.; all boiled between 127° and 129°. The material contained 2·0% of bromine and, although careful refractionation indicated that the brominated ester was concentrated in the higher-boiling fractions, it was not found possible to obtain an ester completely free from bromine. The lowest fraction, b. p. 123—124°/10 mm., containing 0·5% of bromine, was hydrolysed by treatment of 3·8 g. with a solution of potassium hydroxide (2·5 g.) in 95% alcohol (50 c.c.) at the b. p. for 2 hours. Removal of alcohol and acidification gave 3·1 g. (96% of the theoretical amount) of crude α-phenylcrotonic acid, m. p. 130° (136° after crystallisation from 50% alcohol). Ethyl α-phenylcrotonate is described by Dimroth and Feuchter (*Ber.*, 1903, **36**, 2253) as an oil, b. p. 128—131°/15 mm.

Action of Ammonia on α-Bromo-α-phenylbutyryl Bromide.—The acid bromide (3·1 g.) was added slowly with stirring to aqueous ammonia (15 c.c.; *d* 0·880) at 40°. The oil was collected after 1 hour and crystallised from 50% alcohol (yield, 1·2 g. or 75% of the theoretical). The substance melted at 104° and was identical with α-phenylcrotonamide prepared from α-phenylcrotonyl chloride as described below (Found: N, 8·6. Calc.: N, 8·7%). The aqueous mother-liquor from the reaction mixture contained 2 equivs. of bromide ion. This unsaturated amide is probably identical with the amide, m. p. 98—99°, described by Pfeiffer, Engelhardt, and Alfuss (*Annalen*, 1928, **467**, 158).

Action of Urea on α-Bromo-α-phenylbutyryl Bromide.—A mixture of the acid bromide (7·5 g.) and urea (3·0 g.) was heated at 55° for 3 hours. On addition of water an oil was formed which solidified on chilling. This (3·8 g.) was crystallised from alcohol until the m. p. was constant (167°); the material then contained 2·3% of bromine, which could not be diminished by further crystallisation. Analysis indicated that this was substantially α-phenylcrotonylcarbamide (Found: N, 13·5%).

Hydrolysis of Impure α-Phenylcrotonylcarbamide. Isolation of the Pure High-melting Carbamide.—The impure carbamide, m. p. 167°, containing 2·3% of bromine (5 g.) was heated for 12 hours at 50° with a 1% solution of sodium hydroxide (100 c.c.). After cooling, the crystalline solid (A) was removed, and the filtrate acidified with hydrochloric acid. The precipitated solid (B) was collected. The solid A (1·0 g., m. p. 191°) crystallised from alcohol, in which it was sparingly soluble, in colourless needles, m. p. 197°. Analysis showed it to be *α-phenylcrotonylcarbamide* (Found: C, 64·6; H, 6·05; N, 13·6. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%). The solid B (2·5 g., m. p. 126°) was α-phenylcrotonic acid, m. p. 136° after crystallisation from 50% alcohol (Found: equiv., 161. Calc.: equiv., 162).

α-Phenylcrotonamide.—α-Phenylcrotonic acid was converted into the *acid chloride* (b. p. 131°/10 mm.) by treatment with thionyl chloride; yield, 95% (Found: Cl, 20·5. $C_{10}H_9OCl$ requires Cl, 19·6%). Addition of the acid chloride (9 g.) to 15% aqueous ammonia (50 c.c.) gave α-phenylcrotonamide, m. p. 103° after crystallisation from alcohol (Found: N, 8·8. Calc.: N, 8·7%); yield, 88%.

Hydrolysis of α-Phenylcrotonamide.—The amide (2·0 g.) was refluxed for 1 hour with N-sodium hydroxide (100 c.c.). Acidification and ether extraction gave 1·9 g. (95% of the calculated amount) of α-phenylcrotonic acid, m. p. 135° (Found: equiv., 161).

Low-melting (Stable) α-Phenylcrotonylcarbamide.—α-Phenylcrotonyl chloride (9 g.) and urea (7 g.) were mixed and kept at 30° for 24 hours. Water was added at 60° in order to break up the viscous mass. The colourless prisms formed (7·1 g.; 70%) had m. p. 185°, not raised by crystallisation from alcohol (Found: C, 64·7; H, 6·15; N, 13·5. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%). Like its isomeride, this *form* decolorises bromine water on gentle warming. A mixture of the two isomerides shows a considerable depression of m. p.

Hydrolysis of the Two α-Phenylcrotonylcarbamides.—(i) *High-melting (labile) form.* The carbamide (5 g.), m. p. 197°, was refluxed with a 1% solution of sodium hydroxide (100 c.c.) for various periods. After cooling, the unchanged carbamide was collected, and the filtrate treated with hydrochloric acid. The precipitate was in all cases practically pure α-phenylcrotonic acid, m. p. 130°. After 1, 12, and 24 hours the hydrolysis % was 13, 72, and 90 respectively.

(ii) *Low-melting (stable) form.* The carbamide (2 g.), m. p. 185°, was refluxed for 30 minutes with 10% sodium hydroxide solution (20 c.c.); after cooling, acidification, and extraction with ether, 1·45 g. (90% of the calculated amount) of α-phenylcrotonic acid, m. p. 136°, were obtained.

α-Phenylbutyrylcarbamide.—(i) Reduction of either form of α-phenylcrotonylcarbamide with 4% sodium amalgam as described by Newbery (*loc. cit.*) for the reduction of the two α-ethylcrotonylcarbamides gave 85% of the calculated amount of α-phenylbutyrylcarbamide, m. p. 147° after crystallisation from alcohol (Found: N, 13·6, 13·55 in the two cases. Calc.: N, 13·6%). (ii) α-Phenylbutyryl chloride (25 g.) was mixed with urea (25 g.) and heated at 30° for 48 hours. Water was added, and the crystals collected and recrystallised

from alcohol. The m. p. 147° was undepressed by the product from (i). Yield, 17 g., 60% (compare D.R.-P. 249,241).

NN'-*Bis*-(α-*phenylbutyryl*)*carbamide*.—α-Phenylbutyryl chloride (18 g.) and urea (12 g.) were mixed and heated at 90° for 24 hours. After addition of water and cooling, the *carbamide* (12 g.) was obtained; it crystallised from alcohol in colourless plates. m. p. 172° (Found: N, 8·0. $C_{21}H_{24}O_3N_2$ requires N, 8·0%).

Hydrolysis of NN'-*Bis*-(α-*phenylbutyryl*)*carbamide*.—The carbamide (15 g.) was heated with N-sodium hydroxide (50 c.c.) and alcohol (50 c.c.) for 2 hours at 90°. After removal of alcohol, addition of water precipitated α-phenylbutyramide (1 g.), m. p. 85° after crystallisation from alcohol. Acidification of the filtrate gave α-phenylbutyric acid (10 g.), m. p. 38°, identified by its equivalent (Found: 162. Calc.: 164) and by comparison with a genuine specimen.

Bromination of α-*Phenylbutyrylcarbamide*.—Bromine (27 g.) was added to the carbamide (17 g.) suspended in water (130 c.c.) at 20°. The mixture was refluxed and agitated until the bromine had been absorbed. The oil formed solidified on cooling; after being washed with water, dried, and crystallised from 95% alcohol, α-(*bromophenyl*)*butyrylcarbamide* was obtained in colourless plates (10 g.), m. p. 178—179° (Found: N, 10·0; Br, 27·9. $C_{11}H_{13}O_2N_2Br$ requires N, 9·8; Br, 28·1%).

Hydrolysis of α-(*Bromophenyl*)*butyrylcarbamide*.—The bromo-carbamide (2·5 g.) was refluxed with a solution of potassium hydroxide (2·5 g.) in 90% alcohol (25 c.c.) for 3 hours. Removal of alcohol and addition of dilute hydrochloric acid gave an oil, which was extracted in ether, dried (anhydrous sodium sulphate), and recovered (1·8 g.). It solidified on chilling and had m. p. 40—43° after crystallisation from 50% alcohol. Analysis showed it to be an α-(*bromophenyl*)*butyric acid* (Found: Br, 32·4; equiv., 237. $C_{10}H_{11}O_2Br$ requires Br, 32·9%; equiv., 243).

RESEARCH LABORATORIES,
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41. *The Caoutchol Component of Natural Rubber: A Correction.*

By K. C. ROBERTS.

It has proved impossible to isolate from rubber or latex as available in this country materials having the characteristic properties of caoutchol and caoutchene (cf. Roberts, J., 1938, 215, 219) as prepared in the East. Samples of these materials prepared in Malaya have, however, been examined in England by the author and his colleagues. It is reaffirmed that caoutchol is a naturally occurring, oxygenated constituent of rubber, quite distinct from artificially oxidised rubbers, but in the light of the evidence now discussed it is necessary to withdraw the original suggestions (*a*) that the elasticity of rubber is derived essentially from that of its minor constituent caoutchol, and (*b*) that caoutchol has a molecular formula $C_{80}H_{130}(OH)_2$.

THE author recently described a method (J., 1938, 215, 219), developed in Malaya, for separating natural rubber into two main fractions, one containing amongst other things a hydrocarbon which was called "caoutchene," and the other including an oxygenated material which constitutes some 2—5% of natural rubber. The latter, which was named "caoutchol," was described as a non-tacky, freely soluble, highly elastic substance for which the formula $C_{80}H_{130}(OH)_2$ was suggested. "Caoutchene," constituting 87—91% of total rubber and isolated only in a crude state, was described as being tacky, of low tensile strength, and as giving solutions of notably low viscosity, and its elongation under tension was stated not to exceed 200%. It was further suggested that the elasticity of rubber was derived essentially from its minor constituent "caoutchol."

The author has now been able to re-examine the material in collaboration with his colleagues on the staff of the British Rubber Producers' Research Association. Fresh facts have been brought to light, both here and elsewhere, in consequence of which it has been found necessary to amend or withdraw the suggestions originally put forward. Nevertheless it is emphasised that "caoutchol" is a naturally occurring material of real interest, quite distinct from artificially oxidised rubbers.

A critical comment by Kraay and Altman (*Arch. Rubbercultuur*, 1938, 22, 231) claims to show that "caoutchol" is an oxidation product of "caoutchene," first, because increased access of oxygen gave increased yields of the "caoutchol" fraction, and secondly, because further amounts of the "caoutchol" fraction could be obtained by resubmitting the precipitated "caoutchene" to the fractionation procedure. Unfortunately, however, the authors made no attempt to characterise the material contained in the "caoutchol" fractions. They did not attempt to show that it was, in fact, "caoutchol," and not "caoutchol" together with, for example, the somewhat differently constituted oxidation products of the rubber hydrocarbon. Their conclusion, therefore, cannot be accepted as valid.

A further communication, by Haefele and McColm (J., 1939, 676), pointed out that, if care were taken to exclude air, the removal of caoutchol from rubber did not lead to tackiness and loss of elasticity in

the residual crude hydrocarbon. Their evidence, though strong, unfortunately suffers from lack of quantitative data.

Their observation is, however, supported independently by Gee and Treloar (*Trans. Inst. Rubber Ind.*, 1940, **16**, 197), who have shown that fractions of purified rubber hydrocarbon obtained by removal of gummy oxygenated material from natural rubber are still highly elastic and similar in physical properties to total crepe rubber. Moreover, it has been shown by Treloar (*Trans. Faraday Soc.*, 1940, **36**, 538) that it is not necessary to postulate a two-phase system in order to account for the elasticity of natural rubber, and that such elasticity is essentially a property of the long-chain molecules of which rubber is composed. In the light of these publications the author now withdraws his suggestion that the elasticity of rubber is derived essentially from that of its minor constituent "caoutchol."

The author's claim that "caoutchol" purified by hydrolysis is a chemical individual with a formula approximating to $C_{80}H_{130}(OH)_2$ must be withdrawn in the light of the following new evidence, for details of which the author is indebted to the workers named.

(1) "Caoutchol," whether hydrolysed or not, can be fractionated. Dr. G. F. Bloomfield, employing the technique previously applied to rubber (Bloomfield and Farmer, *Trans. Inst. Rubber Ind.*, 1940, **16**, 69), has obtained the following fractions:

Type of caoutchol.	Light petroleum–acetone at 20°.	% dissolved.	Average mol. weight.	Oxygen content, %.
Hydrolysed	50/50 extract A	47	45,000	0·15
	50/50 extract B	16	—	0·1
	55/45 extract	23	93,000	1·6
	Residue (insoluble in light petroleum or in petroleum–acetone)	10	—	6·2
Unhydrolysed	50/50	29·2	20,000	3·95
	52/48	14·6	53,000	1·3
	55/45	16·4		0·9
	60/40	32·2	70,000	1·05

(2) The molecular weight, as determined by Dr. G. Gee, does not agree with the molecular weight required by the formula. Molecular weights of four different samples determined by viscosity methods already described (*Trans. Faraday Soc.*, 1940, **36**, 1162) were 43,000, 47,000, 50,000, and 57,000. The molecular weights of the last two, determined osmotically, were 51,000 and 54,000. These high values cannot be ascribed to association, since the specific viscosity of the first sample in benzene was shown to be almost independent of temperature.

(3) The analytical evidence, by Dr. W. T. Chambers and Dr. F. Hilton, does not point unequivocally to the formula suggested [Found: C, 85·7, 86·5, 86·1, 85·3; H, 11·7, 12·0, 11·8, 11·2; OH (cf. Bolland, *Trans. Inst. Rubber Ind.*, 1941, **17**, 267), 0·48. Calc. for $C_{80}H_{130}(OH)_2$: C, 85·4; H, 11·8; OH, 3·0%].

Nevertheless, as has already been stated, "caoutchol" is a naturally occurring material of considerable interest, differing markedly in physical properties from any artificially oxidised rubber which has been examined in these laboratories. In the first place, Dr. L. R. G. Treloar has shown that, in spite of its low molecular weight, "caoutchol" possesses mechanical properties approximating much more closely to those of total rubber than to those of a degraded rubber of approximately the same molecular weight. Using the methods already applied to rubber (*loc. cit.*; *Trans. Faraday Soc.*, 1941, **37**, 84), Treloar has shown:

(*a*) That the maximum elongation of "caoutchol" is 700% at 25°.

(*b*) That the tensions are only 20—40% lower than those of crepe rubber at corresponding elongations.

(*c*) That the plastic flow at 25° is relatively small, being not more than 6% of the elastic elongation (the corresponding figure for crepe rubber is 2%).

(*d*) That crystallisation of caoutchol commences at 400% elongation and that its birefringence rises to 60 Na wave-lengths per mm. at breaking point. The latter figure is about half the maximum observed with crepe rubber at the same elongation.

In contrast with this, both a rubber hydrocarbon and an artificially oxidised rubber of similar molecular weight (60,000) were observed to be merely sticky gums, without appreciable strength or elasticity. The possession of good rubber-like properties by the low-molecular "caoutchol" is thought to indicate a stronger cohesion between the molecules than occurs in the rubber hydrocarbon, at least at certain points in their length.

Furthermore, Dr. G. A. Jeffrey, over a period of time, has examined the *X*-ray diffraction patterns of a number of samples of "caoutchol" prepared in Malaya. He finds that, when stretched, all the samples give a well-defined fibre diagram identical with that of stretched rubber, but that in the unstretched state they show a diffraction pattern having a narrower halo than that of unstretched rubber and two or more distinct Debye–Scherrer rings. On freezing at 0·5° for several days, "caoutchol" does

not give the powder diagram characteristic of frozen rubber. A summary of his observations on unstretched "caoutchol" is included in the following table of mean values for the glancing angles of the diffraction maxima. Figures in parentheses indicate the number of observations.

"Caoutchol."			"Oxide" fraction of Bloomfield and Farmer.		
Diffuse halo	8° 30′—10° 0′	(4)	Diffuse halo	8° 30′—9° 48′	(3)
Ring 1	10° 46′	(4)	Ring 1	10° 41′	(3)
Ring 2	12° 3′	(4)	Ring 2	11° 58′	(2)
Ring 3	13° 36′	(2)			
Ring 4	17° 53′	(1)			
Ring 5	19° 4′	(2)			
Ring 6	20° 19′	(1)			
Ring 7	21° 43′	(1)			

The series of rings for "caoutchol" is quite distinct from that of frozen raw rubber and indicates a higher degree of regularity than is possessed by amorphous rubber. The precise nature of this structural regularity is not at present known. The rings are completely absent from the photographs of all artificially oxidised rubbers so far examined, but a halo and two rings have been observed in *X*-ray photographs of the "oxide" fraction separable from natural rubber by the technique of Bloomfield and Farmer (*loc. cit.*). Data for the latter are included in the above table, from which it is seen that the photographs resemble those of "caoutchol" in the size of the halo and the position of the rings. They were, however, much less distinct and showed more general diffused scattering. The "oxide" fraction, unlike "caoutchol," is an inelastic gum. T. C. Roberts (*Nature*, **1938**, **141**, 834) has reported the existence of sharp rings in the *X*-ray diffraction pattern of unstretched "caoutchol." Her unpublished data have been examined by Dr. G. A. Jeffrey, who states that they are not significantly different from his own and that he therefore cannot support the suggestions made by her in the publication above referred to.

A sample of "caoutchene" received from Malaya was found by Dr. G. Gee to have a molecular weight of approximately 140,000. Dr. G. A. Jeffrey found that this sample gave *X*-ray data identical with those given by rubber, *i.e.*, the same amorphous pattern when unstretched, the same fibre diagram on stretching, the same crystalline powder ring pattern when frozen. No systematic study of its mechanical behaviour has been undertaken, but its relatively poor elastic properties and its molecular weight, combined with the *X*-ray data, indicate clearly that it is merely a degraded rubber.

The above conclusions are based on evidence obtained from specimens of "caoutchol" and "caoutchene" sent to this country from Malaya. It should be stated that it was found necessary to work with such samples because it has proved impossible to prepare in England materials having all the properties of those prepared in the East.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

Welwyn Garden City, Herts. [*Received, November 25th*, 1941.]

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42. *The Constitution of Agar.*

By W. G. M. Jones and S. Peat.

Evidence is presented that agar is the sulphuric acid ester of a linear polygalactose. The unit-chain is composed of nine residues of *d*-galactose mutually combined by 1 : 3-glycosidic linkages. This chain is terminated at the reducing end by a residue of *l*-galactose, which is united with the rest of the chain by a glycosidic linkage engaging C_4 and not C_3. The *l*-galactose member is esterified at C_6 with sulphuric acid.

This conception of the structure of agar explains the isolation of *l*-galactose from it, the separation of 2 : 4-dimethyl 3 : 6-anhydro-*l*-galactose and 2 : 5-*dimethyl* 3 : 6-*anhydro*-l-*galactonic acid* from methylated agar and also satisfactorily accounts for the absence of sulphuric acid residues from acetylated and methylated agar.

The probable course of the biological synthesis of agar is discussed.

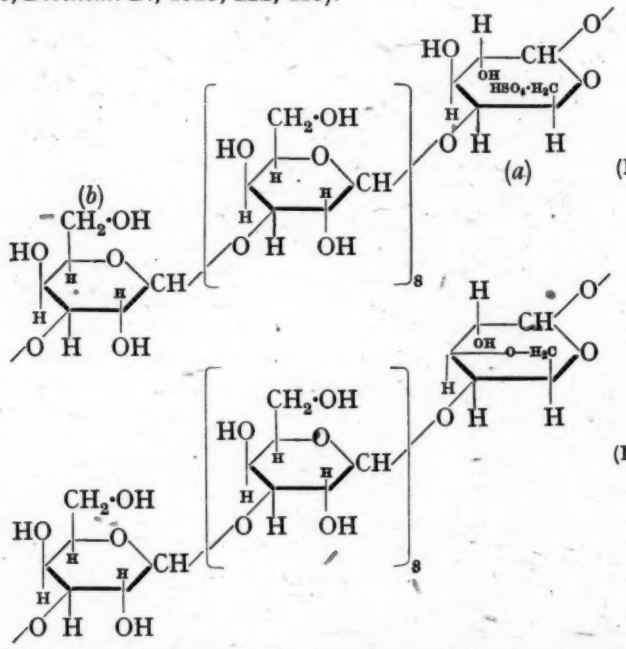
In the past decade progress has been made in the elucidation of the constitution of agar, for which is now proposed a simple structure conforming with the known facts and new directions are suggested along which further investigation may be pursued.

The agar polysaccharide, as it occurs in the plant, is to be envisaged as composed entirely of galactose residues. These are arranged in chains which are themselves repeating units. Each unit-chain consists of approximately nine *d*-galactopyranose residues mutually combined by 1 : 3-glycosidic linkages;

but a further fact of exceptional significance is that this chain is terminated at the reducing end not by a member of the *d*-series but by one residue of *l*-galactopyranose, the glycosidic link in this case involving C_4, and not C_3. Furthermore, the primary alcohol group (C_6) of each *l*-galactose residue is esterified with sulphuric acid. The complete repeating unit is shown in (I).

If the structure (I) were not a repeating unit, but represented the whole molecule of agar, it is clear that methylated agar would contain tetramethyl *d*-galactopyranose as the non-reducing end group. Except in special circumstances detailed below, tetramethyl galactose has not been detected hitherto as a constituent of methylated agar (cf. Percival *et al.*, J., 1937, 1615; 1939, 1844). It is a reasonable assumption, therefore, that (I) is a repeating chain-unit in which the reducing group of the *l*-galactose member, (*a*), provides the point of attachment to a second unit-chain, and this end-to-end attachment is established with the terminal non-reducing *d*-galactose residue, (*b*), of the second chain. The degree of aggregation of the unit-chain is not yet known, but information on this point may be forthcoming from determination of the molecular weight of agar.

Commercial agar, as was established by Neuberg and Ohle (*Biochem. Z.*, 1921, **125**, 311) and confirmed subsequently by others, has sulphuric acid residues present in organic combination. The sulphuric ester is easily hydrolysed by acid or alkali. The formulation suggested for agar, (I), requires a sulphur content of 1·8%. Figures varying from 0·5 to 1·5% are given in the literature for the sulphur content of samples of agar, a variability which may easily be due to the greater or lesser extent of the hydrolysis of sulphate effected during the technical purification of agar, a process which often involves bleaching with chlorine (cf. Lüdtke, *Biochem. Z.*, 1929, **212**, 419).



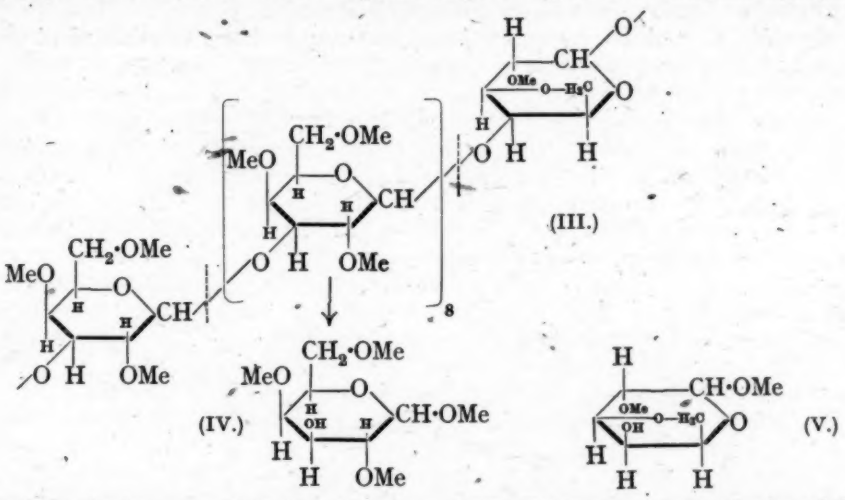
There is reason to affirm that the hydrolysis of a sugar sulphuric ester follows the same course as the hydrolysis of a sugar toluenesulphonic ester, namely, that an anhydro-ring is developed in the sugar residue if a suitably situated hydroxyl group is available. Thus, Percival and Soutar (J., 1940, 1475) have shown that the alkaline hydrolysis of α-methylglucoside sulphate and of α-methylgalactoside sulphate leads, in each case, to the formation of an anhydro-methylhexoside.* In agar, the *l*-galactose sulphate residue is united with the rest of the chain through position 4, and consequently the hydroxyl at C_3 is available for anhydro-ring formation.

It is to be expected, therefore, that the hydrolytic removal of the sulphate group at C_6 would be attended by the formation of a 3 : 6-anhydro-bridge in the *l*-galactose residue, and the repeating unit of agar would assume the form (II).

Neither acetylated nor methylated agar contains sulphur and it is in keeping with the above considerations to assume that during the methylation process the hydrofuranol (*i.e.*, 3 : 6-anhydro) ring appears in the *l*-galactose residue (II) in place of the sulphate grouping (I). On this conception, agar

* (*Note added in proof, March 20th*, 1942.) Duff and Percival have now shown (J., 1941, 830) that the anhydro-methylhexosides formed as described are 3 : 6-anhydro-α-methylglucoside and 3 : 6-anhydro-α-methylgalactoside respectively.

methylated entirely in alkaline solution will have the constitution represented by (III) and the methanolysis of methylated agar will give rise to 2 : 4 : 6-trimethyl *d*-methylgalactoside (IV) and 2-methyl 3 : 6-anhydro-*l*-methylgalactoside (V), the latter representing *ca.* 9% of the methylated polysaccharide.



2 : 4 : 6-Trimethyl *d*-galactose was first isolated from methylated agar by Percival and Somerville (J., 1937, 1615), who showed that this sugar derivative was the chief constituent of the methylated agar hydrolysate, amounting to at least 65% of the whole (see Forbes and Percival, J., 1939, 1846). It is demonstrated thereby that the predominant glycosidic linkages along the chain are at positions 1 and 3 in each pair of such residues which are mutually combined.

The monomethyl anhydro-*l*-methylgalactoside (V) has not yet been isolated, but its presence in the methylated agar hydrolysate has been detected, inasmuch as when the higher-boiling fractions of the hydrolysate are further methylated, crystalline 2 : 4-dimethyl 3 : 6-anhydro-β-*l*-methylgalactoside is obtained (Hands and Peat, *Chem. and Ind.*, 1938, 937; *Nature*, 1938, **142**, 797; Percival, Somerville, and Forbes, *ibid.*, p. 797; Forbes and Percival, *loc. cit.*). The increase of methoxyl content of these higher-boiling fractions by further methylation corresponded with the conversion of a monomethyl into a dimethyl anhydromethylhexoside.

The linkage of the anhydro-*l*-galactose unit to the rest of the chain (II) is regarded as occurring at C_4, since it cannot take place at C_3 or C_6, these positions being occupied by the anhydro-ring, nor yet at C_2 for reasons which will now be outlined.

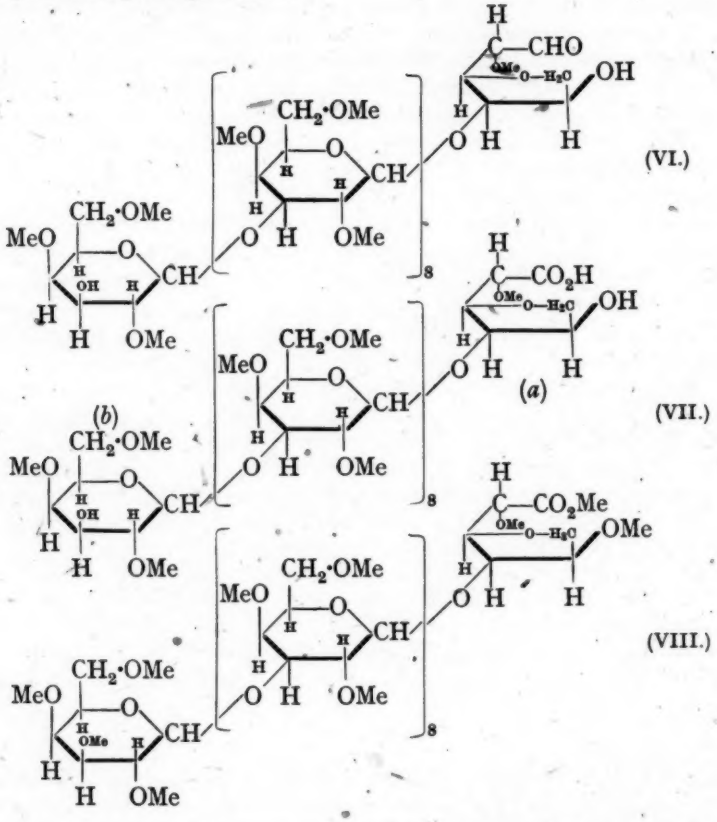
Commercial agar was exhaustively methylated by the direct action of methyl sulphate in alkaline solution. Fractional precipitation of the methylated agar separated it into two main fractions (A and B) distinguished by their ash contents. The fraction (A) with relatively high ash content was dissolved in dilute sulphuric acid and submitted to prolonged dialysis against running tap-water. Although the product of dialysis contained no sulphuric acid residues, its aqueous solution was strongly acid in reaction. The presence of acidic groups was further demonstrated by the fact that the treatment of the dialysed product with diazomethane led to its esterification and a consequent increase in methoxyl content. The extent of this increase, considered together with the results of equivalent determination by alkali titration, indicated the presence in the dialysed product of one carboxyl group to every ten hexose residues.

The question now arose as to the origin of this acidic polysaccharide. It might have been an original constituent of agar, or on the other hand a factitious product formed during the technical preparation of agar or during the processes of methylation and purification of the methylated agar. There are many reasons for adopting the second view.

It has been shown by Haworth, Jackson, and Smith (J., 1940, 625) that the presence together in a hexose of hydrofuranol and pyranose rings confers exceptional properties on the compound, particularly in regard to its sensitivity to acid. The normal stability of the pyranose ring is markedly diminished and it is found, for example, that 2 : 4-dimethyl 3 : 6-anhydro-*d*-methylgalactopyranoside is converted by contact with cold N/10-sulphuric acid into 2 : 4-dimethyl 3 : 6-anhydro-*aldehydo*-*d*-galactose.

Now the *l*-galactose residue in (II) is constituted on precisely this model, and it is to be expected that the effect of acid would be to cause the fission of the glycosidic linkage between two repeating units, the disappearance of the pyranose ring from the *l*-galactose, and the appearance of a free aldehyde group in its place.

If acid conditions are avoided before and during methylation, methylated agar will have the constitution represented by (III), and this is probably a true representation of the fraction (B) with low ash content. On the other hand, if acid conditions supervene after methylation, then the sequence of events just related will occur and the methylated agar will assume the form (VI), which represents it as a single chain of nine 2 : 4 : 6-trimethyl *d*-galactose residues terminated at the reducing end by monomethyl 3 : 6-anhydro-*aldehydo*-*l*-galactose.



If, concurrently, oxidation conditions are present, the reactive aldehydo-group of the *l*-galactose will readily be converted into carboxyl. Such oxidation might conceivably be effected by atmospheric oxygen during the dialysis in acid solution of the methylated agar, which would now be represented by (VII).

If the acid (VII) were submitted to further methylation with methyl iodide and silver oxide, the carboxyl group would be esterified but, in addition, the hydroxyl groups at C_5 of the *l*-galactose residue (*a*) and at C_3 of the terminal *d*-galactose unit (*b*) would be methylated and (VIII) would be formed. This indeed appears to be the effect of methylation with these reagents of the dialysed product (A), for there occurs an increase in methoxyl content (from 33 to 38%) which is larger than can be accounted for by the simple esterification of a carboxyl group, such as diazomethane effects. The complete hydrolysis of the ester (VIII) would yield mainly 2 : 4 : 6-trimethyl *d*-galactose, but there would also be produced tetramethyl *d*-galactose from (*b*), and 2 : 5-dimethyl 3 : 6-anhydro-*l*-galactonic acid from (*a*), the last two in equimolecular proportion.

These predictions were fulfilled in the actual results of our experiments. From the hydrolysate of the ester derived from (A) by the procedure described, there were separated tetramethyl *d*-galactose and a dimethyl anhydrohexonic acid, the latter being isolated as the crystalline amide (m. p. 173°). The constitution of the anhydrohexonic acid was established in the following manner.

The anhydro-ring in this substance has survived repeated treatment with acid and alkaline reagents and is therefore clearly not of the ethylene oxide type. Its stability in fact recalls that of the hydrofuranol type of anhydro-ring and in the absence of evidence to the contrary the description of the substance as a 3 : 6-anhydro-hexonic acid would be justified. Furthermore, since the presence of 3 : 6-anhydro-*l*-galactose in agar has already been proved, the hexonic acid may be particularised as dimethyl 3 : 6-anhydro-*l*-galactonic acid. This assumption finds support in that the rotation of the amide

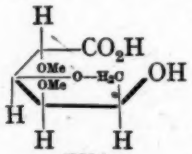
($[\alpha]_D^{19°}$ — 76°) is of the same order and sign as that of the amide derived from 2 : 4-dimethyl 3 : 6-anhydro-*l*-galactonic acid ($[\alpha]_D$ — 74°. Forbes and Percival, *loc. cit.*). The disposition of the methoxyl groups is inferred from the following considerations. There are three possible structures to examine, namely, 2 : 4-dimethyl (IX), 2 : 5-dimethyl (X), and 4 : 5-dimethyl 3 : 6-anhydro-*l*-galactonic acid (XI).

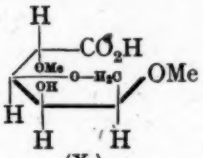
The amide in question gave a negative Weerman test for α-hydroxy-amides, on which ground (XI) is excluded. The amide of (IX) has been shown by Forbes and Percival (*loc. cit.*) to melt at 151°, as does the *d*-isomer prepared by Haworth, Jackson, and Smith (*loc. cit.*). This melting point is 20° lower than that of the amide now isolated and described, and it is improbable that the two are identical. The conclusion must therefore be drawn that the acid isolated in the form of its amide from the acidic polysaccharide constituent of methylated agar is 2 : 5-*dimethyl* 3 : 6-*anhydro*-l-*galactonic acid* (X).

The reason for the description of the mode of union of the *l*-galactose residue in agar with the rest of the chain as a 1 : 4-glycosidic linkage (I and II) is now apparent. The ultimate isolation of 2 : 5-dimethyl 3 : 6-anhydro-*l*-galactonic acid is only explicable on the assumption that the hydroxyl at C_4 of the original *l*-galactose is involved in the chain linkage.

In the foregoing analysis, it has been assumed that the changes leading to the oxidation of agar to an acid polysaccharide occur during the dialysis of the methylated agar, and this is possibly the stage at which oxidation is most marked. But it is obvious that the requisite conditions of acidity and oxidation might be present also in the preparation of commercial agar, and even in its methylation with methyl sulphate, should local acidity develop during this process. The heterogeneity observed in methylated agar might therefore be due to a combination of these causes.

It is known that when a sulphuric ester of a hexose is hydrolysed with alkaline reagents an anhydro-ring is invariably formed if the disposition of the free hydroxyl groups is appropriate. The effect of acid hydrolysing agents has not however been so fully investigated and it is conceivable that acid agents effect normal hydrolysis of the ester without the formation of the anhydro-ring. If that be the case, agar (I) will yield a mixture of *d*- and *l*-galactose when it is resolved into its monosaccharide constituents by hydrolysis with acid. It would thus be possible to explain the isolation of *dl*-galactose acetate from the products of acetolysis of agar (Pirie, *Biochem. J.*, 1936, **30**, 369).


(IX.)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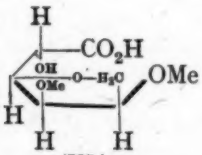
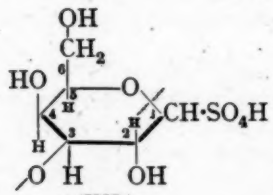

(XI.)

It may well be significant in considering the mode of the biological synthesis of agar that *d*-galactose 1-sulphate substituted at C_3 (XII) is convertible by a simple intramolecular oxidation-reduction change into *l*-galactose 6-sulphate substituted at C_4 (XVI) and the sequence of events involved in such a change could follow as illustrated in (XII)—(XVI).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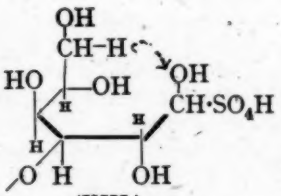
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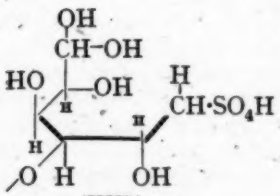
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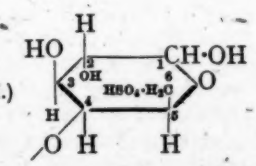
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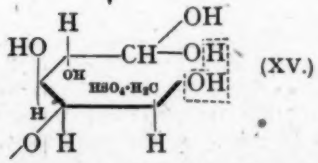
(XV.)

It is not unreasonable, therefore, to suppose that a sulphate fulfils a similar function in the biological synthesis of agar to that of a phosphate in the enzymatic synthesis of starch from glucose 1-phosphate (Hanes, *Proc. Roy. Soc.*, 1940, *B*, **128**, 421; **129**, 174). On this supposition, the initial material in the biological synthesis of agar is *d*-galactose 1-sulphate, from which is formed a chain of *d*-galactose residues combined by 1 : 3-glycosidic linkages. When ten such *d*-galactose members have been united, a change

in the synthetic procedure becomes operative, and the tenth member, bearing its sulphuric acid group, undergoes the intramolecular transformation just described, whereby it is converted into the *l*-galactose residue. In the case of starch, the phosphoric acid, having fulfilled its function, is not retained by the starch, but with agar the sulphuric acid remains, with its orientation readjusted, as an integral part of the molecule.

Experimental.

Methylation of Agar.—Commercial agar (20 g.), dissolved in 15% sodium hydroxide solution (100 c.c.), was stirred at room temperature with methyl sulphate (430 c.c.) and 30% sodium hydroxide solution (1150 c.c.), added during 10 hours. After being heated for 1 hour on a boiling-water bath, the solution was cooled in ice, neutralised with 15% sulphuric acid, and made faintly alkaline. The methylated product was precipitated thereby as a grey powder, which was collected on a linen filter. The methylation was repeated under the same conditions. The third and subsequent methylations were conducted at 45° in the presence of acetone or dioxan. After eight methylations, crude methylated agar was obtained in a granular form.

Fractional precipitation of the methylated agar was carried out on batches of 40 g. Each batch was dissolved by being stirred for 48 hours with 1500 c.c. of alcohol–chloroform (1 : 10). The viscid solution was dried with anhydrous magnesium sulphate (which was removed in the centrifuge) and then treated with increasing volumes of light petroleum. The properties of the fractions so obtained are given in Table I.

Table I.

Batch.	Fraction.	Weight, g.	Ash, %.	OMe, % (corrected for ash).	Batch.	Fraction.	Weight, g.	Ash, %.	OMe, % (corrected for ash).
A	1	2·5	25·8	31·5	C	1	6·5	21·8	30·0
	2	18·5	3·9	33·2		2	4·9	14·8	31·6
	3	6·5	0·02	34·8		3	15·4	2·7	33·7
	4	0·3	0·0	38·4		4	3·3	0·5	34·6
B	1	12·6	17·4	31·0	D	1	9·6	15·6	31·8
	2	2·4	11·5	33·0		2	3·6	11·4	32·4
	3	25·0	2·7	34·1		3	9·8	1·7	32·3
	4	0·8	0·0	35·0		4	3·5	0·0	34·8

Dialysis of Methylated Agar.—All the fractions (Table I) having an ash content of more than 2% were combined (methylated agar A; 86 g.) and submitted to dialysis in batches of 20 g. Similarly, the fractions of low ash content were combined (methylated agar B; 11 g.). The batch for dialysis was dissolved in 2% sulphuric acid by being shaken for 48 hours. A parchment paper membrane was used, and the dialysis against running tap-water continued for 72 hours. The solution was maintained slightly acid by the addition of sulphuric acid in drops until near the end of the dialysis, which was continued until all sulphate ion had been removed. The dialysed solution was then evaporated at 50° and the residue was purified by precipitation from its solution in chloroform–alcohol with light petroleum. The dialysed material had OMe 33·6%, was acid in reaction, and had equivalent (by titration), 1870. The latter figure corresponds to one carboxyl group in ten hexose units.

A small portion of fraction B3 (Table I) was dialysed separately in sulphuric acid and yielded a sample of methylated agar A, which had OMe, 31·6% (ash corrected). Esterification of this sample with diazomethane resulted in a product with a methoxyl content of 32·5% (ash corrected). This increase in methoxyl content corresponds again to one carboxyl group in ten hexose units.

Further Methylation of Methylated Agar A.—The whole of the dialysed material was methylated in batches of 20 g. with methyl iodide and silver oxide. After four treatments the product had OMe, 38·2% (constant value) and showed $[\alpha]_D^{21°}$ − 56·85° (*c*, 0·67 in chloroform). The increase in methoxyl was therefore *ca.* 5%, compared with the increase of 1% produced by diazomethane.

Methanolysis of the Fully Methylated Ester A.—The material (44·0 g.; OMe, 38·2%) was boiled with 2% methyl-alcoholic hydrogen chloride (616 c.c.) until no further change in rotation occurred ($[\alpha]_D$ − 51·8° → + 37·8° in 20 hours). After neutralisation with silver carbonate, the solution was evaporated and the syrupy residue (47·5 g.) was submitted to high-vacuum distillation. It thus became apparent that the methanolysis was far from complete and it was necessary repeatedly to treat with acid methyl alcohol the fraction of the product which did not distil. After four repetitions of this procedure, the undistillable residue was very small and four fractions of distillate were separated, each consisting of a mixture of ester and glycoside. The ester was separated by the treatment of each fraction with saturated barium hydroxide at 80° for 3 hours. The solution was then diluted, and the excess of barium hydroxide removed with carbon dioxide. The residue obtained after evaporation of the solution was dried and exhaustively extracted with boiling dry ether. The extract (N) contained no acidic constituents and the residue (R) was composed chiefly of barium salts.

The barium salts (R) from the four fractions were combined (4·9 g.) and esterified by being boiled for 9 hours with methyl-alcoholic hydrogen chloride (150 c.c.) of concentration sufficient to remove barium as chloride and to leave a 1% solution of hydrogen chloride. After neutralisation with silver carbonate the solution was evaporated, and the residual ester (3·6 g.) extracted with dry ether. Fractional distillation of the ester was only partly successful, and it was necessary to reconvert the ester into the barium salt, which

was again extracted exhaustively with ether. A small amount (0·27 g.) of a non-acidic constituent was thus removed. The residual barium salt was again esterified by treatment with cold methyl-alcoholic hydrogen chloride and subsequently with diazomethane. The ester so obtained (1·4 g.) was separated into three fractions by distillation at 0·03 mm. pressure. The main fraction (2) (0·7 g.) had $[\alpha]_D^{17°} \pm 0°$ (*c*, 0·978 in methyl alcohol); OMe, 44·0% and equivalent, by titration, 253. (Methyl dimethyl anhydrohexonate, $C_9H_{16}O_7$, requires OMe, 39·1% and equivalent 238.)

2 : 5-*Dimethyl* 3 : 6-*Anhydro*-l-*galactonamide*.—The ester fraction 2 (49 mg.) was dissolved in dry methyl alcohol (5 c.c.) and the solution after saturation with ammonia was kept at 0° for 3 days. Evaporation of the alcohol left a syrup which crystallised. The crystals were separated by trituration with dry acetone and the product was recrystallised from acetone (yield of amide, 20% of weight of ester). The *amide* had m. p. 173° and $[\alpha]_D^{12°} -75·7°$ (*c*, 1·56 in water) (Found: C, 47·2; H, 7·4; N, 7·4; OMe, 30·5. $C_8H_{15}O_5N$ requires C, 46·8; H, 7·3; N, 6·8; OMe, 30·2%).

The amide gave a negative Weerman test for α-hydroxy-amides.

Examination of the Neutral Glycoside Mixture (*N*).—The material was fractionally distilled at 0·02—0·03 mm. over a range of 96—180° (bath temp.), and the following fractions were collected:

Fraction	1	2	3	4	5	6	7	8	9	10
Weight (g.)	3·2	3·5	2·5	6·6	3·8	6·4	0·7	3·6	1·5	0·8
OMe, %	60·4	57·2	52·4	—	—	—	—	48·0	43·1	41·4
$[\alpha]_D^{20°}$	+114·5°	—	—	—	—	+52·8°	—	+34·5°	+1·0°	—

Fractions 2 to 6 were crystalline or partly crystalline.

Fraction 1 was not hydrolysed by 0·1N-sulphuric acid at 100°, but hydrolysis took place when the acid strength was increased to N ($[\alpha]_D + 124° \rightarrow +100°$ in 9 hours). The solution was neutralised and evaporated, and the residue extracted with ether. The extract yielded crystalline tetramethyl *d*-galactopyranose, m. p., alone and in admixture with an authentic specimen, 73—74° ($[\alpha]_D^{20°} + 119·3°$, equilibrium value in water).

Fractions 2—6 consisted mainly of 2 : 4 : 6-trimethyl αβ-methyl-*d*-galactoside (cf. Percival *et al.*, *loc. cit.*), which was also found in fraction 8. It was separated in crystalline form, m. p. 80° (softening at 65°) alone or in admixture with an authentic specimen. It had $[\alpha]_D^{20°} + 57·6°$ in water (*c*, 0·64) (Found: C, 50·5; H, 8·3; OMe, 53·2. Calc. for $C_{10}H_{20}O_6$: C, 50·8; H, 8·5; OMe, 52·5%).

The authors are greatly indebted to Professor W. N. Haworth, F.R.S., for his interest in this work. They wish also to thank the Department of Scientific and Industrial Research for a maintenance grant to one of them (W. G. M. J.).

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43. *The Constitution of Yeast Ribonucleic Acid. Part V. Synthesis of Yeast Adenylic Acid.*

By Geoffrey R. Barker and J. Masson Gulland.

Yeast adenylic acid has been synthesised by phosphorylation of adenosine.

The method devised by Gulland and Hobday (J., 1940, 746) for phosphorylating nucleosides at the 3-position of the carbohydrate radical with phosphoryl chloride and baryta has now been applied to the conversion of adenosine into yeast adenylic acid (adenosine 3-phosphate). The identity of the product with an authentic sample was demonstrated by comparison of their specific rotations and rates of dephosphorylation by acid, and by the failure of the 5-nucleotidase of Russell's viper venom (Gulland and Jackson, *Biochem. J.*, 1938, **32**, 597) to effect dephosphorylation.

Experimental.

A mixture of adenosine (1 g.), finely powdered (60 mesh) barium hydroxide (30 g.), and water (25 c.c.) in a pulversing mill containing agate balls was cooled in ice and salt, and the mill and freezing mixture were shaken mechanically. A solution of phosphorus oxychloride (3·8 g.) in ether (5 c.c.) was added during an hour and the shaking was continued for a further 2 hours. The mixture was diluted with water and neutralised to litmus by passage of carbon dioxide, and the precipitate collected and washed free from chloride with water (ppt. A).

The filtrate was freed from chloride by the addition of a little acetic acid and silver acetate solution, and after removal of the silver chloride, the solution was concentrated to about 25 c.c. under reduced pressure. The addition of neutral lead acetate produced no precipitate, indicating that no nucleotide was present, but the addition of ammonia caused the formation of a slight precipitate, from which a small quantity of adenosine was recovered.

Precipitate A was extracted six times with boiling water (75 c.c. each), and the combined extracts were

concentrated to small volume under reduced pressure and mixed with excess of lead acetate. The precipitated lead salt was collected, suspended in hot water (150 c.c.), and decomposed with hydrogen sulphide, and the solution was filtered from lead sulphide, concentrated to small volume under reduced pressure, and poured into alcohol. After standing overnight in the refrigerator, the nucleotide (0·14 g.) was centrifuged, and the products from several experiments were combined, reconverted into the lead salt, and the filtrate resulting from its decomposition as before was concentrated and poured into alcohol. The yeast adenylic acid was collected and washed with alcohol and ether (Found in material dried at 110°: N, 20·6; P, 8·9. Calc. for $C_{10}H_{14}O_7N_5P$: N, 20·2; P, 8·9%). In 2% sodium hydroxide solution (*c* 0·664), it had $[\alpha]_D^{20}$ — 60·9°; Levene (*J. Biol. Chem.*, 1920, **41**, 483) gives — 59·5°, Embden and Schmidt (*Z. physiol. Chem.*, 1929, **181**, 135) — 56·0°, both in the same solvent.

A mixture of this acid (10 mg.), Russell's viper venom (2 mg.), and p_H 8·6 borate buffer (5 c.c.) was diluted to 10 c.c. with water, containing toluene, and incubated at 37°. Samples (2 c.c.) were withdrawn at intervals for the colorimetric estimation of inorganic phosphate, but none was liberated during 2 hours.

The acid (9·081 mg.) was dissolved in water (15·0 c.c.), and portions (2·0 c.c.) were mixed with an equal volume of N/5-sulphuric acid, sealed in glass tubes, and heated at 100°. Tubes were withdrawn at intervals, and the free phosphate in their contents determined colorimetrically. The percentage dephosphorylation, calculated on the basis of the inorganic phosphate liberated and the total phosphorus content of the initial solution, was compared with that which occurred in an identical experiment with authentic yeast adenylic acid.

Time, hrs.	1	2	4	8
Dephosphorylation of synthetic adenylic acid, % ...	35·3	58·4	77·4	91·5
,, ,, yeast ,, ,, , % ...	33·2	58·8	74·7	90·6

We acknowledge gratefully a research grant from Imperial Chemical Industries Ltd.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 2nd,* 1942.]

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44. *The Constitution of Purine Nucleosides. Part X. A New Synthesis of Xanthine and Attempted Syntheses of Xanthine Glucosides from Glyoxalines.*

By WILLIAM E. ALLSEBROOK, J. MASSON GULLAND, and LEONARD F. STORY.

A new synthesis of xanthine is described, starting from a glyoxaline derivative. Experiments are recorded in which it was sought to utilise this or a similar method for the synthesis of purine nucleosides with the glycosidic radical in the position occupied in the naturally occurring nucleosides. These experiments failed, because it was not found possible to introduce the glycosidyl radical into the glyoxaline molecule, but successful parallel research using methyl iodide instead of the acetylated bromo-sugar indicated which glyoxalines would have yielded glycosidyl derivatives correctly, or incorrectly, oriented for nucleoside synthesis.

ADENINE-9-GLUCOSIDE and guanine- and hypoxanthine-glucosides, all prepared from the same precursor, are the only known synthetic purine glycosides in which the sugar occupies the same position as do the glycosidic radicals of the naturally occurring nucleosides. The determination of the structure of adenine-9-glucoside (Gulland and Story, J., 1938, 259) depends on the comparison of ultra-violet absorption spectra, and although no question arose of the efficacy of this method in this and other cases it was desirable if possible to confirm its results by an independent means, such as an unequivocal synthesis. For this the starting material must contain either a pyrimidine or a glyoxaline ring, but not both, so that the need for decision between the tautomeric 7- and 9-positions of the purine as the point of entry of the glycosidic radical does not arise. The former alternative was investigated by Gulland and Macrae (J., 1933, 662), who tried unsuccessfully to obtain theophylline-9-glucoside by condensing 1 : 3-dimethyluramil and tetra-acetylglucose *iso*thiocyanate. The present communication records experiments following the latter alternative.

Two syntheses of purines from glyoxalines are known, both yielding 7-substituted derivatives. Sarasin and Wegmann (*Helv. Chim. Acta*, 1924, **7**, 713) converted 4-amino-1-methylglyoxaline-5-carboxyamide into 7-methylxanthine (heteroxanthine) by heating with ethyl carbonate, and Montequi (*Chem. Zentr.*, 1927 ii, 1351) condensed 4-amino-5-cyano-2-methyl-1-ethylglyoxaline with urethane and hydrolysed the product to 8-methyl-7-ethylxanthine. Fargher and Pyman (J., 1919, **115**, 217) and Windaus and Langenbeck (*Ber.*, 1923, **56**, 683) attempted to synthesise xanthine from 4(5)-aminoglyoxaline-5(4)-carboxylic acid, but were obliged to abandon the scheme owing to experimental difficulties.

We have now converted the hydrochloride of the methyl ester of this aminoglyoxalinecarboxylic acid into *methyl 4(5)-ureidoglyoxaline-5(4)-carboxylate* by means of potassium cyanate, and the corresponding *acid* (I), obtained by hydrolysis, yielded xanthine when heated with hydrochloric acid.

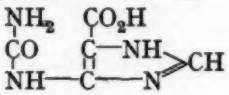
Glycosidic radicals can be substituted for the tautomeric hydrogen atom of a glyoxaline ring by inter-

action of the silver salt with the acetobromo-sugar, and the point of entry may be determined by methylation, fission of the glycosidyl-glyoxaline methiodide by hydrolysis, and identification of the methylated glyoxaline (Gulland and Macrae, *loc. cit.*).

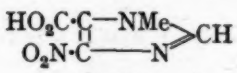
Experiments were made to unite the foregoing synthesis of xanthine with this method of introducing the glycosidyl radical into a suitable glyoxaline in a subsequently determined position. These failed because tetra-acetobromoglucose did not react with the silver salt of the methyl ester of 4(5)-nitroglyoxaline-5(4)-carboxylic acid or of 4(5)-nitro-5(4)-styrylglyoxaline, from which the preceding acid is obtained by oxidation. It was then shown that, even if the condensation had succeeded in the case of the ester, the product would ultimately have led to 7-glucosidylxanthine, because in a comparable reaction methyl iodide transformed the silver salt of the ester into *methyl 4-nitro-1-methylglyoxaline-5-carboxylate*, of which the constitution was ascertained by hydrolysis to the acid (II), obtained by oxidation of *4-nitro-5-styryl-1-methylglyoxaline*, which in turn was prepared from 4-nitro-1: 5-dimethylglyoxaline and benzaldehyde. The orientation here is such as to lead to heteroxanthine.

4(5)-Nitro-5(4)-styrylglyoxaline, on the other hand, would have been a potential starting point, because methyl iodide transformed its silver salt into *5-nitro-4-styryl-1-methylglyoxaline*, also obtained from 5-nitro-1 : 4-dimethylglyoxaline and benzaldehyde. This was oxidised by permanganate to *5-nitro-1-methylglyoxaline-4-carboxylic acid* (III), in which the orientation is such as to lead to 9-methylxanthine.

In view of the lack of success in these reactions with tetra-acetobromoglucose, attention was directed to Sarasin and Wegmann's purine synthesis, and its applicability to the production of a 9-substituted xanthine was tested with positive results by methylation of the silver salt of 4(5)-nitroglyoxaline-5(4)-carboxyamide into *5-nitro-1-methylglyoxaline-4-carboxyamide*, which was hydrolysed to the corresponding acid (III) by Bouveault's method. Unfortunately all attempts failed to effect interaction of the silver salt of the amide with tetra-acetobromoglucose. It is hoped to continue these experiments if opportunity arises.



(I.)



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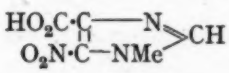

(III.)

Experimental.

4(5)-*Nitro*-5(4)-*methylglyoxaline*.—Methylglyoxaline was prepared from methylglyoxal essentially as described by Gulland and Macrae (*loc. cit.*), but in the larger scale reactions of the present research the purification of the crude base through its silver derivative was omitted, distillation under reduced pressure providing adequate refinement.

Methylglyoxaline was slowly dissolved in nitric acid (*d* 1·42; 2 parts) cooled in a freezing mixture, and concentrated sulphuric acid was gradually added to the cooled solution. The mixture was heated in a boiling brine bath for 2 hours, then boiled in an oil-bath for ½ hour, cooled, and poured on ice. Fargher and Pyman (*loc. cit.*) record that the nitro-derivative separated at this stage, but we found it necessary to neutralise (cooling) with concentrated sodium hydroxide solution. Nitromethylglyoxaline then separated; it crystallised from water in colourless prisms, m. p. 248° as recorded by Fargher and Pyman.

In the hope of avoiding the tedious decomposition of the zinc salt of methylglyoxaline with hydrogen sulphide, followed by the lengthy evaporation of the resulting solution (see Gulland and Macrae, *loc. cit.*), an attempt was made to nitrate the zinc salt directly by the procedure just outlined. Crude nitromethylglyoxaline, m. p. 215°, was produced, but the difficulties encountered in its adequate purification rendered the proposed short-cut uneconomical.

4(5)-*Nitro*-5(4)-*styrylglyoxaline*.—A mixture of nitromethylglyoxaline (20 g.), freshly distilled benzaldehyde (40 g.), and piperidine (2 c.c.) was refluxed for 2 hours at 150—160°. When cold, the resulting golden-yellow mass was extracted with a little hot alcohol to remove tarry by-products, extracted repeatedly with boiling water, in which it was insoluble, crystallised from glacial acetic acid, and washed with acetone. Nitrostyrylglyoxaline (18 g.) formed golden-yellow needles, m. p. 303° (decomp.) (Found: N, 19·5. Calc. for $C_{11}H_9O_2N_3$: N, 19·5%). Windaus and Langenbeck (*loc. cit.*) state that the compound decomposes from 220° onwards.

The aqueous extracts (above) deposited, on cooling, crystalline nitromethylglyoxaline, m. p. 244° (Found: N, 33·1. Calc. for $C_4H_5O_2N_3$: N, 33·1%), which was used in another preparation. It was preferable both here and in the later cases to work under the conditions stated and to recover unchanged material than to raise the temperature; under such conditions the reaction was more complete and little or no nitromethylglyoxaline was recovered, but a large amount of tar was produced and purification of the product was difficult.

4(5)-*Nitro*-5(4)-3' : 4'-*methylenedioxystyrylglyoxaline* (2·5 g.), prepared from nitromethylglyoxaline (3 g.) and piperonal (8·4 g.) under analogous conditions to those described above, formed yellow-brown plates, m. p. 288° (decomp.) (Found: N, 16·1. $C_{12}H_9O_4N_3$ requires N, 16·2%).

4(5)-*Nitroglyoxaline*-5(4)-*carboxylic Acid and its Methyl Ester*.—Powdered (80 mesh sieve) potassium permanganate (40 g.) was added gradually to a mechanically stirred solution of nitrostyrylglyoxaline (20 g.) in

acetone (200 c.c.) cooled in ice-water. The manganese dioxide sludge was collected and thoroughly extracted with hot water, and the solution, rendered just acid to Congo-red with hydrochloric acid, was evaporated to dryness under reduced pressure. The residue was extracted with carbon tetrachloride in a Soxhlet apparatus for about 30 minutes to remove benzoic acid; ether was found to dissolve some of the nitroglyoxalinecarboxylic acid, and removal of benzoic acid by sublimation was accompanied by partial decomposition of the desired acid.

The nitroglyoxalinecarboxylic acid, left undissolved by carbon tetrachloride, had m. p. 302—303° (decomp.) when crystallised from water (yield, 40%) (Found: N, 26·7. Calc. for $C_4H_3O_4N_3$: N, 26·7%). A small further quantity could sometimes be isolated from the acetone fraction of the oxidation. Windaus and Langenbeck (*loc. cit.*) claim theoretical yields by oxidising nitrostyrylglyoxaline in water, but we have never succeeded in repeating those, and the above method was found more convenient.

Several experiments were carried out in the hope of condensing *p*-nitrosodimethylaniline with nitromethylglyoxaline, since the resulting Schiff's base could be expected to yield nitroglyoxaline aldehyde by acid hydrolysis, and this would readily undergo oxidation to give the acid. Some interaction probably took place under the influence of piperidine or of zinc chloride, but since no pure product could be isolated and not inconsiderable amounts of nitromethylglyoxaline were recovered, the attempt was abandoned.

The methyl ester, colourless plates, m. p. 212—213°, from alcohol (Found: N, 24·6. Calc. for $C_5H_5O_4N_3$: N, 24·6%), was readily obtained from the pure acid by esterification for 1 hour with methyl alcohol (20 parts) containing 5% of dry hydrogen chloride (Windaus and Langenbeck, *loc. cit.*) and partial concentration of the solution. When working on a larger scale, however, it was found convenient to esterify directly the mixture of acid and potassium chloride left from the Soxhlet extraction with carbon tetrachloride, concentrating to dryness the methyl-alcoholic hydrogen chloride solution after the esterification, and adding water, in which the ester was insoluble, to dissolve potassium chloride. In the attempted synthetical experiments the silver salt of the ester was prepared in aqueous alcoholic solution with ammonia and silver nitrate, in order to facilitate its being dried. All attempts failed to condense the dried silver salt with tetra-acetobromoglucose in boiling xylene (Gulland and Macrae, *loc. cit.*; Fischer and Helferich, *Ber.*, 1914, **47**, 210), and the use of the ester itself in acetone in presence of alkali or silver carbonate (Robertson and Robinson, J., 1926, 1715) was equally unsuccessful.

Reduction of the ester to the hydrochloride of methyl 4(5)-aminoglyoxaline-5(4)-carboxylate, m. p. 215° (Found: N, 23·3. Calc. for $C_5H_7O_2N_3$,HCl: N, 23·7%), was effected by hydrogen and palladised charcoal (Windaus and Langenbeck, *loc. cit.*).

Methyl 4(5)-*Ureidoglyoxaline*-5(4)-*carboxylate*.—Solutions of the amino-ester hydrochloride (2 g.) and potassium cyanate (1·8 g.; 2 mols.), each in water (20 c.c.), were mixed, heated on the water-bath for 15 minutes, and cooled. The resulting curdy solid was collected, and a further amount was thrown down by acidifying the filtrate with acetic acid. The combined products were purified by solution in dilute aqueous ammonia (charcoal) and reprecipitation with acetic acid, or by crystallisation from a large volume of water. The *ester* formed a microcrystalline (polarising microscope) powder, m. p. 213° (Found: N, 30·2. $C_6H_8O_3N_4$ requires N, 30·4%). An ammoniacal solution of the ester yielded a curdy white precipitate of the silver salt with ammoniacal silver nitrate solution.

A warm solution of the ester in dilute hydrochloric acid deposited, on cooling, the *hydrochloride*, m. p. 208°, as a microcrystalline powder (Found: N, 25·6. $C_6H_8O_3N_4$,HCl requires N, 25·4%), which tended to lose hydrogen chloride when heated. The picrate, m. p. 208°, separated when aqueous solutions of the ester and picric acid were mixed.

4(5)-*Ureidoglyoxaline*-5(4)-*carboxylic Acid*.—The ester was not hydrolysed by concentrated hydrochloric acid at 100° in 1 hour. A solution of the ester (0·3 g.) in N/2-sodium hydroxide (20 c.c.) was heated at 100° for 1½ hours and neutralised to methyl-orange with hydrochloric acid; the solid which separated was purified by reprecipitation from ammonia solution with acetic acid. The *acid* decomposed at a high temperature without melting (Found: N, 33·1. $C_5H_6O_3N_4$ requires N, 32·9%), and dissolved readily in sodium carbonate solution.

Xanthine.—Ureidoglyoxalinecarboxylic acid was heated with boiling hydrochloric acid (equal parts of acid and water) for 15 minutes. The liquid was made alkaline with ammonia, then acid with acetic acid; xanthine separated as a cream-coloured powder. It was purified by boiling a solution in a slight excess of dilute aqueous ammonia; xanthine then separated in very sparingly soluble flakes (Found in material dried at 110°: N, 36·7. Calc. for $C_5H_4O_2N_4$: N, 36·8%), which gave a strong murexide reaction. The identity of this material was confirmed in two ways. (i) It acted as a substrate in the anærobic system methylene-blue–xanthine dehydrogenase of milk, the times required for decolourisation being the same as those when authentic xanthine was used in similar conditions. (ii) The perchlorates of the synthetic and the authentic xanthine, prepared by dissolving these in hot 30% perchloric acid and cooling the solutions, had the same microscopic appearance and both sintered and darkened at 260° (Biltz and Beck, *J. pr. Chem.*, 1928, **118**, 166).

4-*Nitro*-1 : 5-*dimethylglyoxaline and* 5-*Nitro*-1 : 4-*dimethylglyoxaline*.—Pyman (J., 1922, **121**, 2616) has described these compounds and their preparation from the dimethylglyoxalines (J., 1910, **97**, 1814). The following are additional useful methods, nitromethylglyoxaline being used as starting material.

(i) The silver salt of 4(5)-nitro-5(4)-methylglyoxaline, prepared with aqueous alcoholic ammonia and silver nitrate, was freed from alcohol and water by means of the pump and then by distilling benzene from its suspension in that solvent. Methyl iodide (1·25 mols.) was added, and the mixture boiled for 8 hours; a further

quantity of methyl iodide was added, and the heating repeated. The benzene was distilled from the silver precipitates, which were thoroughly extracted with hot water, and the combined extracts were made alkaline and extracted with chloroform. Distillation of this solvent yielded 4-nitro-1 : 5-dimethylglyoxaline, m. p. 160° after crystallisation from water (Found : N, 29·6. Calc. for $C_5H_7O_2N_3$: N, 29·8%); Pyman (*loc. cit.*) records m. p. 160—161° (corr.).

(ii) A mixture of 4(5)-nitro-5(4)-methylglyoxaline (20 g.), benzene (100 c.c.), and pure methyl sulphate (1·25 mols. ; 19 c.c.) was refluxed for 3 hours. When cold, the benzene was decanted, and the residual pasty mass stirred with acetone; the solid was collected, washed with acetone, and crystallised from alcohol. The *methosulphate* formed prisms or fern-like needles, m. p. 143—144° (Found : N, 16·5; S, 12·5. $C_6H_{11}O_6N_3S$ requires N, 16·6; S, 12·6%). An aqueous solution of the methosulphate was made strongly alkaline with sodium hydroxide and extracted with chloroform; distillation of the dried extract yielded 5-nitro-1 : 4-dimethylglyoxaline, m. p. 55—56°, or 57—58° when recrystallised from light petroleum (Found : N, 30·0. Calc. for $C_5H_7O_2N_3$: N, 29·8%). Pyman (*loc. cit.*) records m. p. 57—58° (corr.).

4-Nitro-5-styryl-1-methylglyoxaline.—A mixture of 4-nitro-1 : 5-dimethylglyoxaline (2 g.), freshly distilled benzaldehyde (3·6 g.), and piperidine (0·3 c.c.) was refluxed at 150—160° for 2 hours; when cold, the product was stirred with alcohol to remove tar and extracted with hot water (see below). The residue, the *styryl* compound, crystallised from ethyl acetate in yellow plates, m. p. 150—151° (Found : N, 18·0. $C_{12}H_{11}O_2N_3$ requires N, 18·3%), which were sparingly soluble in hot water and alcohol. The yield was 40—50%, but the aqueous extract (see above) yielded unchanged nitrodimethylglyoxaline, which was used for subsequent preparations.

Methyl 4-Nitro-1-methylglyoxaline-5-carboxylate.—The silver salt of methyl 4(5)-nitroglyoxaline-5(4)-carboxylate, largely freed from water by being stirred with alcohol, was dried by distillation of much of the benzene from its suspension in sulphur-free benzene. Methyl iodide (1·5 mols.) was added, and the mixture refluxed for 8 hours; methyl iodide (1 mol.) was added, and boiling continued for 8 hours. The benzene was removed by distillation, and the residue extracted with hot alcohol. Evaporation of the alcohol left a solid, which was stirred with dilute sodium carbonate solution in order to remove traces of unmethylated ester; the insoluble *methyl 4-nitro-1-methylglyoxaline-5-carboxylate* crystallised from alcohol in prisms or in fern-like needles, m. p. 128—129° (Found : N, 22·7. $C_6H_7O_4N_3$ requires N, 22·7%).

4-Nitro-1-methylglyoxaline-5-carboxylic Acid.—(i) Hydrolysis of the methyl ester by 10% sodium hydroxide solution for 5 minutes at 50° and acidification with acetic acid yielded large prisms, m. p. 160°, which were identified as 4-nitro-1-methylglyoxaline-5-carboxylic acid (Sarasin and Wegmann, *loc. cit.*, give m. p. 160°) by mixed m. p. with a sample prepared from the styryl compound by oxidation, and also by conversion into 4-nitro-1-methylglyoxaline, m. p. 135°, through elimination of carbon dioxide at 160°.

(ii) 4-Nitro-5-styryl-1-methylglyoxaline was oxidised in acetone solution with powdered potassium permanganate exactly as described for 4(5)-nitro-5(4)-styrylglyoxaline. The product formed prisms, m. p. 160°. The yields were not good and the method (i) above is to be regarded as preferable.

4-Nitro-1-methylglyoxaline.—A slight excess of alcoholic silver nitrate solution was added slowly to a stirred solution of 4(5)-nitroglyoxaline (Fargher and Pyman, *loc. cit.*) (2·2 g.) in aqueous alcoholic ammonia. The gelatinous precipitate of silver salt soon became granular; it was collected, washed with alcohol, and freed from alcohol and water by distillation of its suspension in benzene. Methyl iodide (2·5 g.) was added, and the mixture refluxed for 8 hours; this treatment was repeated twice. The benzene and methyl iodide were distilled off, and the residue extracted with hot water, from which 4-nitro-1-methylglyoxaline, m. p. 135°, separated in needles after concentration (Hazeldine, Pyman, and Winchester, J., 1924, **125**, 1431, record m. p. 133—134°). None of the isomeric 5-nitro-1-methylglyoxaline was found.

5-Nitro-4-styryl-1-methylglyoxaline.—(i) A mixture of 5-nitro-1 : 4-dimethylglyoxaline (10 g.), benzaldehyde (20 c.c.), and piperidine (1 c.c.) was refluxed at 150—160° for 2 hours. The cooled product was mixed with light petroleum (b. p. 60—80° ; 60 c.c.) to remove the excess of benzaldehyde and left for 12 hours until deposition of yellow prisms had ceased. The light petroleum was decanted, and the residue washed with a little alcohol to remove tar and crystallised from ethyl acetate. The *styryl* compound formed golden-yellow, prismatic needles, m. p. 214—215° (Found : N, 18·1. $C_{12}H_{11}O_2N_3$ requires N, 18·3%), which were more readily soluble in alcohol and acetone than the isomeric 4-nitro-5-styryl-1-methylglyoxaline. The yields did not exceed 25—30%.

(ii) The silver salt of 4(5)-nitro-5(4)-styrylglyoxaline, prepared from aqueous alcoholic ammonia and silver nitrate, was dried by distillation of its suspension in benzene, and then refluxed with methyl iodide as described in other cases. The benzene was distilled off, and the residue extracted with hot ethyl acetate, from which the styryl compound crystallised in good yield after concentration; it was identified by mixed m. p.

5-Nitro-1-methylglyoxaline-4-carboxylic Acid.—(i) Oxidation of the corresponding styryl compound in acetone by powdered potassium permanganate was carried out in the usual way; the *acid* crystallised from water in prisms or hexagonal plates, m. p. 165° (Found in material dried at 110° : N, 24·5. $C_5H_5O_4N_3$ requires N, 24·5%. Found in material dried in a vacuum : N, 21·5; loss at 110°, 11·8. $C_5H_5O_4N_3,1\frac{1}{2}H_2O$ requires N, 21·5; loss, 12·3%).

(ii) 5-Nitro-1-methylglyoxaline-4-carboxyamide withstood hydrolysis by concentrated hydrochloric acid in a sealed tube for 3 hours at 160°, but was successfully hydrolysed by Bouveault's method (*Bull. Soc. chim.*, 1892, **9**, 368). Barium nitrite (220 mg.), dissolved in the minimum quantity of water, was added drop by drop

to a solution of the amide (146 mg.) in 90% sulphuric acid (4 c.c.) cooled in ice. The mixture was left at room temperature for 24 hours and poured into much water, and sulphate ions were exactly removed from the hot solution by means of barium acetate solution. The barium sulphate was centrifuged and the clear, colourless solution, containing neither barium nor sulphate ions, was concentrated under reduced pressure to about 10 c.c. A good yield of the acid separated in hexagonal plates, m. p. 165°.

Specimens of the acid prepared by either method evolved carbon dioxide briskly as they melted, and the residues crystallised at once on cooling and then melted at 54—55°, being thus identified as 5-nitro-1-methylglyoxaline; Hazeldine, Pyman, and Winchester (*loc. cit.*) give m. p. 55°.

5-Nitro-1-methylglyoxaline-4-carboxyamide.—The silver salt of 5(4)-nitroglyoxaline-5(4)-carboxyamide (Windaus and Langenbeck, *loc. cit.*), prepared in aqueous alcoholic ammonia and silver nitrate, was freed from alcohol and water by distillation of its suspension in benzene. Methyl iodide (about 2 mols.) was then added, and the mixture refluxed for 8 hours; more methyl iodide was added, and the boiling continued for 24 hours in all. The benzene was removed by distillation, the residue extracted with hot water, and the extract concentrated under reduced pressure to small volume. The solid which crystallised was stirred with dilute aqueous ammonia to remove traces of unchanged amide, m. p. 291°; the residual *5-nitro-1-methylglyoxaline-4-carboxyamide* crystallised from water in both needles and dog-tooth shaped crystals, m. p. 234° (Found: N, 33·1. $C_5H_6O_3N_4$ requires N, 32·9%). The two crystalline forms appeared in the same solutions, and were separated by hand and proved to be identical by mixed m. p. The isomeric 4-nitro-1-methylglyoxaline-5-carboxyamide (Sarasin and Wegmann, *loc. cit.*) has m. p. 257—258°.

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45. *The Bromination of* 1 : 5-*Dihydroxy- and* 1 : 5-*Diacetoxy-naphthalene,* 5-*Methoxy-*1-*naphthol, and* 1 : 5-*Dimethoxynaphthalene.*

By A. H. CARTER, E. RACE, and F. M. ROWE.

Dibromination of 1 : 5-dihydroxynaphthalene, 1 : 5-diacetoxynaphthalene, 5-methoxy-1-naphthol and 1 : 5-dimethoxynaphthalene has been studied, and the orientation of the products established by oxidation either to bromohydroxynaphthaquinones or to bromomethoxyphthalic anhydrides. Thus, 1 : 5-dihydroxynaphthalene yields 2 : 6-dibromo-1 : 5-dihydroxynaphthalene; 1 : 5-diacetoxynaphthalene yields 2 : 4-*dibromo*-5-*acetoxy*-1-*naphthol*; 5-methoxy-1-naphthol yields 2 : 8-*dibromo*-5-*methoxy*-1-*naphthol*; and 1 : 5-dimethoxynaphthalene yields 4 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene.*

ACCORDING to Wheeler and Ergle (*J. Amer. Chem. Soc.*, 1930, **52**, 4872), bromination of 1 : 5-dihydroxynaphthalene in cold glacial acetic acid gives a mixture of dibromo- and tribromo-1 : 5-dihydroxynaphthalene. The former was stated to be the 2 : 6-dibromo-derivative, since oxidation with chromic acid removed no bromine and resulted in the formation of a dibromohydroxynaphthaquinone which formed an ester with pyroboroacetic acid and was therefore a *p*-quinone. Further, this quinone condensed with aniline with elimination of one bromine atom and formation of 6-bromo-2-anilino-5-hydroxy-1 : 4-naphthaquinone. As well as confirming these results, we have obtained further proof that the bromine atoms are in different rings and in the *o*-positions with respect to the hydroxy-groups, as oxidation of the dibromodihydroxynaphthalene monomethyl ether (III) with chromic acid gave a *dibromomethoxy*-1 : 4-*naphthaquinone* (XIV). Hence, dibromination of 1 : 5-dihydroxynaphthalene in acetic acid yields 2 : 6-dibromo-1 : 5-dihydroxynaphthalene (I), m. p. 224° (decomp.). Methylation of (I) gave 2 : 6-dibromo-1 : 5-dimethoxynaphthalene (II), m. p. 160°, and 2 : 6-dibromo-5-methoxy-1-naphthol (III), m. p. 150°.

By the bromination of 1 : 5-diacetoxynaphthalene in cold glacial acetic acid, Willstätter and Schuler (*Ber.*, 1928, **61**, 362) obtained a dibromo-monoacetyl-1 : 5-dihydroxynaphthalene, m. p. 165·5°, yielding on hydrolysis a dibromo-1 : 5-dihydroxynaphthalene, m. p. 147·5°, which, without submitting any evidence, they stated to be 4 : 8-dibromo-1 : 5-dihydroxynaphthalene. This method of brominating 1 : 5-diacetoxynaphthalene in our hands led to the isolation of a *dibromo-monoacetyl*-1 : 5-*dihydroxynaphthalene* (IV), m. p. 175°, converted by hydrolysis into a dibromo-1 : 5-dihydroxynaphthalene (VII), m. p. 153°. On oxidising (IV) with chromic acid, we obtained a *monobromo-5-acetoxy*-1 : 4-*naphthaquinone* (XV) owing to the elimination of a bromine atom in the *p*-position to the hydroxy-group. Methylation of (IV), followed by hydrolysis of the acetyl group, gave a *dibromo-5-methoxy*-1-*naphthol* (VI), which was converted by oxidation with alkaline permanganate into a *dibromomethoxyphthalic anhydride* (XIX), thus proving that both the bromine atoms are in the same ring in the naphthalene nucleus. Consequently, the orientation of the bromine atoms given by Willstätter and Schuler is incorrect, and the dibromo-1 : 5-dihydroxy-

naphthalene, m. p. 153°, is actually 2 : 4-dibromo-1 : 5-dihydroxynaphthalene (VII). Methylation of (VII) gave 2 : 4-*dibromo*-1 : 5-*dimethoxynaphthalene* (VIII), m. p. 88°.

Bromination of 5-methoxy-1-naphthol in carbon tetrachloride with 1 mol. of bromine gave a *monobromo-5-methoxy-1-naphthol* (IX), m. p. 95°, which, on further bromination with 1 mol. of bromine, yielded a dibromo-5-methoxy-1-naphthol (X), m. p. 130°. The latter was converted by oxidation with chromic acid into a *dibromo-5-methoxy*-1 : 4-*naphthaquinone* (XVII), and by oxidation with permanganate into a *monobromomethoxyphthalic anhydride* (XVIII). Both oxidations establish that the bromine atoms are in different rings of the naphthalene nucleus and, since compound (X) is not identical with 2 : 6-dibromo-5-methoxy-1-naphthol (III), it must be 2 : 8-*dibromo-5-methoxy-1-naphthol*, methylation of which gave 2 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene* (XI), m. p. 84°.

Finally, from the bromination of 1 : 5-dimethoxynaphthalene in carbon tetrachloride with 2 mols. of bromine, a dibromo-1 : 5-dimethoxynaphthalene, m. p. 187°, was isolated. Since this compound is not identical with any of the three isomeric dibromo-1 : 5-dimethoxynaphthalenes (II), (VIII) and (XI), it is clearly 4 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene* (XII).

Experimental.

2 : 6-*Dibromo*-1 : 5-*dihydroxynaphthalene* (I).—To a solution of 1 : 5-dihydroxynaphthalene (20 g.) in glacial acetic acid (700 c.c.) at 80°, a solution of bromine (39 g.) in glacial acetic acid (50 c.c.) was added during 30 mins. (Wheeler and Ergle, *loc. cit.*). On standing, pale green needles (29 g.; 73%) separated, which, when recrystallised from glacial acetic acid, formed colourless needles, m. p. 224° (decomp.) (Found: C, 37·9; H, 2·3; Br, 50·2. Calc. for $C_{10}H_6O_2Br_2$: C, 37·75; H, 1·9; Br, 50·3%). On acetylation with acetic anhydride in pyridine, the diacetate, which recrystallised from chloroform–ether in colourless needles, m. p. 225°, was obtained.

2 : 6-*Dibromo*-1 : 5-*dimethoxynaphthalene* (II).—The compound (I) (1 g.) was dissolved in sodium hydroxide solution (10 c.c., 2·5%) and warmed to 60°. Excess of methyl sulphate was added and, after shaking for 10 mins., the precipitate was collected and recrystallised three times from alcohol, forming colourless needles, m. p. 160°.

2 : 6-*Dibromo-5-methoxy*-1-*naphthol* (III).—When the alkaline filtrate from (II) above was acidified with hydrochloric acid, a white precipitate separated; recrystallised twice from alcohol, it formed colourless needles, m. p. 150°.

2 : 4-*Dibromo-5-acetoxy*-1-*naphthol* (IV).—Bromine (7 g.) in glacial acetic acid (12 c.c.) was added dropwise during 30 mins. to a solution of 1 : 5-diacetoxynaphthalene (5 g.) in cold glacial acetic acid (180 c.c.) (compare Willstätter and Schuler, *loc. cit.*). After 16 hrs., 2 : 4-*dibromo-5-acetoxy*-1-*naphthol* separated as a crystalline solid (3·8 g.; 48%), which was recrystallised from benzene, forming colourless prisms, m. p. 175° (Found: C, 40·5; H, 2·15; Br, 43·95. $C_{12}H_8O_3Br_2$ requires C, 40·0; H, 2·2; Br, 44·4%). Acetylation with acetic anhydride in pyridine gave 2 : 4-dibromo-1 : 5-diacetoxynaphthalene, which crystallised from alcohol in long, pale yellow needles, m. p. 131°, and which Willstätter and Schuler erroneously regarded as the 4 : 8-isomeride.

2 : 4-*Dibromo-5-acetoxy*-1-*methoxynaphthalene* (V).—To a solution of 2 : 4-dibromo-5-acetoxy-1-naphthol (3 g.) in methyl alcohol (20 c.c.) and ether (25 c.c.) cooled to − 15°, was added an ethereal solution of diazomethane, prepared by the interaction of potassium hydroxide solution (10 c.c., 50%) and nitrosomethylurea (5 g.). After 3 hrs., the evolution of nitrogen having ceased, the solution was concentrated to half volume; 2 : 4-*dibromo-5-acetoxy*-1-*methoxynaphthalene* separated as a crystalline solid (2 g.; 64%), which was recrystallised from carbon tetrachloride, forming colourless needles, m. p. 121° (Found: C, 41·6; H, 2·7. $C_{13}H_{10}O_3Br_2$ requires C, 41·7; H, 2·7%).

6 : 8-*Dibromo-5-methoxy*-1-*naphthol* (VI).—A suspension of compound (V) (0·9 g.) in aqueous sodium hydroxide (30 c.c., 10%) was refluxed for 2 hrs. until a clear solution was obtained. Water (200 c.c.) was added, and the solution acidified with hydrochloric acid. After 16 hrs., 6 : 8-*dibromo-5-methoxy*-1-*naphthol* separated as a colourless solid (0·7 g.; 92%), which was recrystallised from aqueous methyl alcohol, forming colourless needles, m. p. 112° (Found: C, 39·45; H, 2·55. $C_{11}H_8O_2Br_2$ requires C, 39·8; H, 2·4%).

2 : 4-*Dibromo*-1 : 5-*dihydroxynaphthalene* (VII).—2 : 4-Dibromo-5-acetoxy-1-naphthol (1 g.) was hydrolysed by dissolving it in aqueous sodium hydroxide (100 c.c., 0·4%) and leaving the deep brown solution overnight in a vacuum desiccator. Excess of hydrochloric acid was then added, and the precipitated 2 : 4-dibromo-1 : 5-dihydroxynaphthalene recrystallised from acetone; it formed colourless needles, m. p. 153°.

2 : 4-*Dibromo*-1 : 5-*dimethoxynaphthalene* (VIII).—An ethereal solution of diazomethane, prepared by the action of potassium hydroxide solution (12 c.c., 50%) on nitrosomethylurea (4 g.), was added to a well-cooled solution of compound (VII) (2 g.) in ether (50 c.c.). After 16 hrs., the solution was concentrated and allowed to cool. 2 : 4-*Dibromo*-1 : 5-*dimethoxynaphthalene* separated; after crystallising twice from methyl alcohol, it formed colourless needles, m. p. 88° (0·1 g.; 4·6%) (Found: C, 41·9; H, 2·8; Br, 45·65. $C_{12}H_{10}O_2Br_2$ requires C, 41·6; H, 2·9; Br, 46·25%).

2-*Bromo-5-methoxy*-1-*naphthol* (IX).—Bromine (4·6 g.) in carbon tetrachloride (10 c.c.) was added to a solution of 5-methoxy-1-naphthol (5 g.) in carbon tetrachloride (100 c.c.) at 70°. After 18 hrs., the colourless

solution was concentrated and allowed to cool. 2-*Bromo*-5-*methoxy*-1-*naphthol* separated in pale yellow crystals (2·4 g.; 33%), which, when recrystallised twice from ligroin, formed colourless needles, m. p. 95° (Found : C, 51·9; H, 3·6; Br, 31·3. $C_{11}H_9O_2Br$ requires C, 52·2; H, 3·55; Br, 31·6%).

2 : 8-*Dibromo*-5-*methoxy*-1-*naphthol* (X).—Bromine (18·2 g.) in carbon tetrachloride (20 c.c.) was added to a solution of 5-methoxy-1-naphthol (10 g.) in carbon tetrachloride (250 c.c.) at 70°. After 16 hrs., the solution was boiled (charcoal), concentrated to 100 c.c., and allowed to cool. 2 : 8-*Dibromo*-5-*methoxy*-1-*naphthol* separated in yellow prisms, m. p. 130° (10·8 g.; 57%) (Found : C, 40·9; H, 2·7; Br, 48·0. $C_{11}H_8O_2Br_2$ requires C, 39·8; H, 2·4; Br, 48·2%). Acetylation with acetic anhydride in boiling pyridine yielded 2 : 8-*dibromo*-1-*acetoxy*-5-*methoxynaphthalene*, colourless needles, m. p. 133° (Found : C, 41·45; H, 2·7. $C_{13}H_{10}O_3Br_2$ requires C, 41·7; H, 2·7%).

2 : 8-*Dibromo*-1 : 5-*dimethoxynaphthalene* (XI).—Methyl sulphate (2 g.) was added to a solution of compound (X) (1 g.) in aqueous sodium hydroxide (200 c.c., 0·125%) a few drops at a time, with shaking between the additions. The solution was warmed to 30° and shaken for 30 mins., and the dark coloured precipitate (1 g.; 96%) collected; after recrystallising three times from methyl alcohol, 2 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene* was obtained in colourless needles, m. p. 84° (Found : C, 40·8; H, 3·2; Br, 46·6. $C_{12}H_{10}O_2Br_2$ requires C, 41·6; H, 2·9; Br, 46·25%).

4 : 8-*Dibromo*-1 : 5-*dimethoxynaphthalene* (XII).—Bromine (8·5 g.) in carbon tetrachloride (10 c.c.) was added during 15 mins. to a solution of 1 : 5-dimethoxynaphthalene (5 g.) in carbon tetrachloride (120 c.c.) at 70°. After refluxing for 30 mins., the solution was concentrated to 50 c.c. and allowed to cool. 4 : 8-*Dibromo*-1 : 5-*dimethoxynaphthalene* separated; after crystallising twice from carbon tetrachloride, it formed colourless leaflets, m. p. 187° (2 g.; 22%) (Found : Br, 46·3. $C_{12}H_{10}O_2Br_2$ requires Br, 46·25%).

2 : 6-*Dibromo*-5-*hydroxy*-1 : 4-*naphthaquinone* (XIII).—A solution of chromium trioxide (20 g.) in water (20 c.c.) was added to a suspension of 2 : 6-dibromo-1 : 5-dihydroxynaphthalene (10 g.) in cold glacial acetic acid (200 c.c.) (Wheeler and Ergle, *loc. cit.*). A vigorous reaction occurred and the temperature rose to 85°; after 10 mins., the solution was cooled. The brown crystalline solid which separated was recrystallised, first from alcohol and then from acetic acid; it formed dark red needles, m. p. 202° (1·3 g.; 12·5%) (Found : Br, 47·95.. Calc. for $C_{10}H_4O_3Br_2$: Br, 48·2%).

6-*Bromo*-2-*anilino*-5-*hydroxy*-1 : 4-*naphthaquinone*.—Aniline (1·5 g.) was added to compound (XIII) (0·5 g.) in absolute alcohol (70 c.c.). After refluxing for 5 mins., the solution was allowed to cool; dark lustrous prisms (0·4 g.; 77%) then separated. These were twice recrystallised from alcohol, forming dark red prisms, m. p. 249° (Found : Br, 23·4. Calc. for $C_{16}H_{10}O_3NBr$: Br, 23·25%).

2 : 6-*Dibromo*-5-*methoxy*-1 : 4-*naphthaquinone* (XIV).—2 : 6-Dibromo-5-methoxy-1-naphthol (0·95 g.) was suspended in cold glacial acetic acid (10 c.c.), and a solution of chromium trioxide (2 g.) in water (6 c.c.) added. The mixture was stirred rapidly and warmed to 80°; a vigorous reaction occurred. The crystalline solid (0·4 g.; 40%) which separated on cooling, crystallised from alcohol in bright yellow needles, m. p. 177° (Found : Br, 45·8. $C_{11}H_6O_3Br_2$ requires Br, 46·25%).

2-*Bromo*-5-*acetoxy*-1 : 4-*naphthaquinone* (XV).—Chromium trioxide (5 g.), dissolved in water (10 c.c.), was added to a suspension of 2 : 4-dibromo-5-acetoxy-1-naphthol (5 g.) in cold glacial acetic acid (20 c.c.). The temperature rose to 40°; after the vigorous reaction had subsided, the solution was boiled and then allowed to cool. The deposited crystals (1·5 g.; 37%) were washed with ligroin and dried; 2-*bromo*-5-*acetoxy*-1 : 4-*naphthaquinone* crystallised from alcohol in bright yellow needles, m. p. 158° (Found : Br, 27·3. $C_{12}H_7O_4Br$ requires Br, 27·1%).

2-*Bromo*-5-*methoxy*-1 : 4-*naphthaquinone* (XVI).—A solution of chromium trioxide (5 g.) in water (10 c.c.) was added to a suspension of 2-bromo-5-methoxy-1-naphthol (2 g.) in cold glacial acetic acid (25 c.c.). After 10 mins., the solution was cooled and diluted with water and the crystalline 2-*bromo*-5-*methoxy*-1 : 4-*naphthaquinone* (0·9 g.; 43%) which separated was recrystallised twice from alcohol, forming bright yellow needles, m. p. 134° (Found : Br, 29·8. $C_{11}H_7O_3Br$ requires Br, 29·95%).

2 : 8-*Dibromo*-5-*methoxy*-1 : 4-*naphthaquinone* (XVII).—A suspension of 2 : 8-dibromo-5-methoxy-1-naphthol (3 g.) in cold glacial acetic acid (40 c.c.) was vigorously stirred, and a solution of chromium trioxide (6 g.) in water (12 c.c.) added rapidly. The temperature rose to 40°, the suspended solid dissolved, and in a few minutes dark coloured crystals (2 g.; 64%) separated. Recrystallisation from alcohol gave 2 : 8-*dibromo*-5-*methoxy*-1 : 4-*naphthaquinone* in dark reddish-brown needles, m. p. 199° (Found : C, 38·2; H, 1·8; Br, 45·8. $C_{11}H_6O_3Br_2$ requires C, 38·15; H, 1·75; Br, 46·25%).

Oxidation of 2 : 8-*Dibromo*-5-*methoxy*-1-*naphthol with Permanganate. Isolation of* 5-*Bromo*-6-*methoxyphthalic Anhydride* (XVIII).—A solution of 2 : 8-dibromo-5-methoxy-1-naphthol (40 g.) in aqueous sodium hydroxide (60 g. of sodium hydroxide in 1330 c.c. of water) was heated to the b. p. in 30 mins., during which time potassium permanganate (120 g.) was added in portions. After boiling for 15 mins., the residual permanganate was destroyed with sodium sulphite, and manganese dioxide filtered off and extracted with boiling water (1000 c.c.). Hydrogen peroxide (150 c.c., 100 vol.) was added to the united filtrate and extract, and the solution concentrated to 500 c.c. After cooling and acidification with hydrochloric acid, the product was extracted with ether (450 c.c.), the extract dried over sodium sulphate, and the solvent removed. The residual yellow oil set to a solid (14 g.) when left overnight in a vacuum desiccator. The solid was covered with ether (100 c.c.); the undissolved residue (6 g.), when recrystallised three times from glacial acetic acid, gave 5-*bromo*-6-*methoxyphthalic anhydride* (4 g.) in colourless needles, m. p. 212° (Found : C, 42·4; H, 2·1; Br, 31·3.

$C_9H_5O_4Br$ requires C, 42·0; H, 1·95; Br, 31·1%). It was insoluble in water, did not react with sodium bicarbonate solution, and gave the fluorescein test when fused with resorcinol.

5-Bromo-6-methoxyphthalanil.—A solution of aniline (0·2 g.) in acetic acid (5 c.c.) was added to a solution of 5-bromo-6-methoxyphthalic anhydride (0·5 g.) in boiling glacial acetic acid (10 c.c.), and the mixture refluxed for 5 mins. and allowed to cool. The *phthalanil*, when recrystallised twice from glacial acetic acid, formed colourless needles, m. p. 232° (0·5 g.; 77%) (Found: C, 54·5; H, 2·85; N, 4·8. $C_{15}H_{10}O_3NBr$ requires C, 54·2; H, 3·0; N, 4·2%).

Oxidation of 6 : 8-*Dibromo-5-methoxy-1-naphthol with Permanganate. Isolation of* 3 : 5-*Dibromo-6-methoxyphthalic Anhydride* (XIX).—A solution of 6 : 8-dibromo-5-methoxy-1-naphthol (21 g.) in aqueous sodium hydroxide (60 g. of sodium hydroxide in 800 c.c. of water) was oxidised with potassium permanganate (63 g.), the conditions and method of isolation of the product being similar to those in the case of compound (XVIII) above. The solid (15 g.) was covered with ether (50 c.c.); the undissolved residue, when recrystallised twice from ether, gave 3 : 5-*dibromo-6-methoxyphthalic anhydride* (2·8 g.) in long, colourless, prismatic needles, m. p. 140° (Found: C, 32·7; H, 1·55; Br, 47·85. $C_9H_4O_4Br_2$ requires C, 32·15; H, 1·2; Br, 47·6%), with similar properties to those of compound (XVIII).

3 : 5-*Dibromo-6-methoxyphthalanil* crystallised from glacial acetic acid in long colourless needles, m. p. 191° (Found: C, 43·8; H, 2·3; N, 3·8; Br, 38·65. $C_{15}H_9O_3NBr_2$ requires C, 43·8; H, 2·2; N, 3·4; Br, 38·9%).

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46. *Anti-bacterial Substances allied to Sulphanilamide.*

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A series of substances has been prepared to test the effects on anti-bacterial activity, when various substituents, mostly of a non-basic character, are introduced into the molecule of sulphanilamide. It is shown that such modifications, in contrast with those induced by the use of certain basic substituents, usually result at best in the retention of the original activity.

IT is now well established that compounds represented by the general formula $NH_2 \cdot C_6H_4 \cdot SO_2X$, where NH_2 and SO_2X are in the *para*-position relative to each other, are potent anti-bacterial agents. Such activity is exhibited *in vitro* when X = OH, as in sulphanilic acid, and is greatly enhanced when X = NH_2, as in sulphanilamide, and is then shown *in vivo*.

This activity is greatly enhanced when X is a 2-aminopyridine (sulphapyridine), 2-aminothiazole (sulphathiazole), 2-aminopyrimidine (sulphadiazine) or a guanidine (sulphaguanidine) residue and is to some extent specialised. The four substances resulting from these substitutions have all been used clinically with success. In general, such secondary toxic effects as they exhibit are of a mild order and respond readily to treatment. Bieter *et al.* (*J. Amer. Med. Assoc.*, 1941, **116**, 2231) found that, in chickens, sulphanilamide and the sulphanilyl derivatives of 2-aminopyridine and 2-aminothiazole, as well as other compounds of this group, produced nervous effects due to a chronic cumulative concentration of the drug in the peripheral nerves.

When X = $C_6H_4 \cdot NH_2$, joined through carbon, the resulting product is 4 : 4′-diaminodiphenylsulphone, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot NH_2$, which is probably the most potent anti-bacterial agent of this group, but, as its acute toxicity is high, it has not been used clinically. Also, when it is fed to rats for long periods, peripheral neuritis is observed. In Schiff's bases prepared from this sulphone (Wellcome Foundation Ltd., Henry and Gray, Brit. Pat. 491,265; Buttle, Dewing, Foster, Gray, Smith, and Stephenson, *Biochem. J.*, 1938, **32**, 1101) both kinds of toxic effects are reduced, and in at least two of its derivatives, sodium 4 : 4′-di-γ-phenylpropylaminodiphenylsulphonetetrasulphonate, $C_{30}H_{28}O_{14}N_2S_5Na_4,10H_2O$ (*loc. cit.*), and sodium 4 : 4′-bisvaleramidodiphenylsulphonedi-δ-carboxylate, $NaO_2C \cdot [CH_2]_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot [CH_2]_4 \cdot CO_2Na$ (Wellcome Foundation Ltd., Henry, Gray, and Platt, Brit. Pat. 531,571), the acute toxicity is negligible and with them it has not been possible to produce neuritis in rats. Both these drugs show promise as means of utilising the remarkable anti-bacterial activity of the sulphone.

Although the compounds of this group already evolved have provided the physician with effective means of dealing in dramatic fashion with a number of intractable diseases of bacterial origin, there is still room for improvement and for an extension of their range of therapeutic activity. This justifies further systematic, exploratory work by the chemist and the biologist, both on compounds closely related to the effective substances already known and on compounds allied to these in general structure but with other substituents. The present paper is an essay in this direction. As the compounds described are largely derivatives of sulphanilamide, it will be convenient in referring to them to adopt the nomenclature

suggested by Crossley, Northey, and Hultquist (*J. Amer. Chem. Soc.*, 1938, **60**, 2217) whereby substitution in the nuclear amino-group is indicated by N^4 and in the NH_2 of the sulphonamido-group by N^1.

In the four effective therapeutic agents referred to above it will be noticed that the substituents introduced are all basic in character and it is of interest to investigate the effects of introducing non-basic groups at N^1 or N^4 or in both positions simultaneously. A number of such derivatives have been made, and their anti-bacterial action determined by one of us (D. S.). The results are summarised in the table.

TABLE.

No.	Name.	Formula.	Anti-bacterial action *in vivo*.
1	N^4-Benzoylsulphanilamide	$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$	Inactive
2	N^1N^4-Dibenzoylsulphanilamide	$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH\cdot CO\cdot C_6H_5$	Slightly less active than sulphanilamide (strep.); inactive (pneumo.)
3	Sulphanilylmyristamide	$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot CO\cdot C_{13}H_{27}$	As active as sulphanilamide (strep.); inactive (pneumo.)
4	Sulphanilyladipamide	$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot CO\cdot [CH_2]_4\cdot CO_2H$	One-tenth as active as sulphanilamide
5	Sulphanilylchaulmoogramide	$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot CO\cdot [CH_2]_{12}\cdot C_5H_7$	As active as sulphanilamide (strep.); very slightly active (pneumo.)
6	Disulphanilylethyleneguanidine	$C_3H_5N_3(SO_2\cdot C_6H_4\cdot NH_2)_2$	One-tenth as active as sulphanilamide (strep.); one-sixth and one-tenth as active as sulphapyridine (pneumo. and staph. respectively)
7	Sulphanilylglutamic acid	$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$	Inactive (strep., pneumo.)
8	Sulphanilylaminoethylpyridinium bromide	$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_2H_4(C_5H_5N)Br$	Inactive
9	4-Benzylideneaminobenzenesulphonylglycine	$C_6H_5\cdot CH{:}N\cdot C_6H_4\cdot SO_2\cdot NH\cdot CH_2\cdot CO_2H$	Inactive
10	2′-Acetoxymercuri-3′-hydroxybenzylidenesulphanilamide	$C_6H_3(OH)(HgO_2C\cdot CH_3)\cdot CH{:}N\cdot C_6H_4\cdot SO_2\cdot NH_2$	Slightly less active than sulphanilamide (strep.); inactive (pneumo., staph.)
11	8-Quinolyl *p*-nitrophenyl ether	$C_9H_6N\cdot O\cdot C_6H_4\cdot NO_2$	Inactive (strep., pneumo.)
12	4-*p*-Nitrophenoxybenzenesulphonamide	$NO_2\cdot C_6H_4\cdot O\cdot C_6H_4\cdot SO_2\cdot NH_2$	Inactive (strep., pneumo., staph.)
13	4 : 4′-Bis-(*p*-nitrobenzamido)diphenylsulphone	$SO_2(C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2)_2$	One-hundredth as active as sulphanilamide (strep.); inactive (pneumo., staph.)
14	2-Pyrrolidone-5-carboxyamino-3′-methylbenzene-*x*-sulphonamide	$C_4H_6ON\cdot CO\cdot NH\cdot C_6H_3\cdot (CH_3)\cdot SO_2\cdot NH_2$	One-tenth as active as sulphanilamide (strep.); one-tenth as active as sulphapyridine (pneumo.); inactive (staph.)
15	2-(2′-Pyrrolidone-5′-carboxy-4″-aminobenzenesulphonamido)-pyridine	$C_4H_6ON\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_5H_4N$	Inactive (pneumo., staph.)
16	Diphenylsulphone-4 : 4′-bisazo-β-naphthol	$SO_2(C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH)_2$	Inactive (strep., pneumo.)
17	2 : 2′-Dipyridylsulphone	$C_5H_4N\cdot SO_2\cdot C_5H_4N$	Stimulated pneumococci *in vitro*; inactive (strep.)
18	N^4-Quininoylsulphanilamide	$CH_3\cdot O\cdot C_9H_5N\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$	Inactive (strep., pneumo., staph.)
19	1-Phenyl-2 : 3-dimethyl-5-pyrazolone-*x*-sulphonamide	$C_5H_7ON_2\cdot C_6H_4\cdot SO_2\cdot NH_2$	Less than one-tenth as active as sulphanilamide (strep.); inactive (pneumo., staph.)
20	N^4-Dihydrochaulmoogrylsulphanilamide	$C_5H_9\cdot [CH_2]_{12}\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$	One-hundredth as active as sulphanilamide (strep.); inactive (pneumo., staph.)
21	Diphenylsulphone-4 : 4′-bisazosalicylic acid	$SO_2[C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H]_2$	As active as sulphanilamide (strep.), as active as sulphapyridine (pneumo.), inactive (staph.)
22	Sodium 2-aminopyridine-*N*-methylenebisulphite	$C_5H_4N\cdot NH\cdot CH_2\cdot SO_3Na$	Inactive (strep., pneumo.)
23	Ethyl *p*-nitrobenzenesulphinate	$NO_2\cdot C_6H_4\cdot SO\cdot O\cdot C_2H_5$	One-tenth as active as sulphanilamide (strep.); inactive (pneumo.); trace of activity (staph.)
24	*p*-Nitrobenzenesulphenamide	$NO_2\cdot C_6H_4\cdot S\cdot NH_2$	Less active than sulphanilamide (strep.); trace of activity (pneumo.), less active than sulphapyridine (staph.)
25	4-Nitrobenzenesulphon-4′-nitroanilide	$NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot NO_2$	Trace of activity (strep.); inactive (pneumo., staph.)
26	4-(*p*-Nitrobenzenesulphonamido)-4′-nitrodiphenyl sulphide	$NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot S\cdot C_6H_4\cdot NO_2$	Trace of activity (strep.); inactive (pneumo., staph.)

Substitution in the N^4-position of an acyl group (Nos. 1, 14, 18, 20) or an arylidene group (Nos. 9, 10) for hydrogen led to a decrease in, or disappearance of, activity even when the substituent was a mercurated organic radical (No. 10) known to show marked bactericidal action.

Substitution in position N^1 on the contrary causes no diminution in activity (Nos. 3, 5) so long as a simple, monocarboxylic acid residue is the substituent and such substitution is even sufficient to neutralise the disadvantageous effect of acyl substitution in position N^4 (cf. Nos. 1 and 2). With a dicarboxylic acid, one carboxyl group being left free (No. 4), activity is much reduced and when both are left free (No. 7) the product is inactive.

The remaining items in the table illustrate several points of general interest.

It is a common experience that the accumulation of two or more potentially active substituents in one molecule generally produces an inactive substance, or at least leads to a reduction in activity (see Nos. 6, 15).

The two *p*-nitrophenyl ethers (Nos. 11, 12) were made in consequence of the observation by Buttle *et al.* (*Biochem. J.*, 1938, **32**, 1101) that 4 : 4′-dinitrodiphenyl ether has a slight protective activity, but it was not found in these. The nitro-group appears, from the relative inactivity of 4 : 4′-dinitrodiphenylsulphone (Buttle *et al.*, *Lancet*, 1937, i, 1331), to have little useful therapeutic effect in comparison with the amino-group, and the low activity of Nos. 23, 24, and 26 may be due in part to this fact.

No chemotherapeutical investigation seems to be complete without an inexplicable contrast, which in this case is provided by Nos. 16 and 21, the former being inactive, whereas the latter retains the action of sulphanilamide on the streptococcus and is also as active as sulphapyridine against the pneumococcus. Excluding No. 21, none of the 26 substances dealt with in this paper was sufficiently promising in these bacteriological tests to be worth detailed pharmacological investigation, but a careful biochemical comparison of Nos. 16 and 21 might yield results of scientific interest, which are much needed if the present haphazard methods of chemotherapeutical investigation are to be replaced by a more rational procedure.

Experimental.

N^4-Benzoyl- and N^1N^4-Dibenzoyl-sulphanilamide.—Sulphanilamide (30 g.) was dissolved in 2·5N-sodium hydroxide (150 c.c.) and shaken with benzoyl chloride (25 c.c.). A cream-coloured precipitate of *N^4-benzoylsulphanilamide* separated which, after being washed, dried, and crystallised from 16 parts of pyridine, had m. p. 284° (Found : N, 10·3; S, 11·6. $C_{13}H_{12}O_3N_2S$ requires N, 10·1; S, 11·6%).

The alkaline liquor on acidification gave an orange-coloured precipitate. This was crystallised by solution in 30 parts of alcohol and dilution with an equal volume of water. The crystals were recrystallised from alcohol, *N^1N^4-dibenzoylsulphanilamide* being obtained in white crystals, m. p. 268—270° (Found : N, 7·3; S, 8·3. $C_{20}H_{16}O_4N_2S$ requires N, 7·4; S, 8·4%).

The mono- and the di-benzoyl derivative do not dissolve readily in sodium hydroxide solution except on warming; sparingly soluble sodium salts are then formed. The dibenzoyl derivative is readily soluble in dilute aqueous ammonia.

N^1N^4-Dibenzoylsulphanilamide was more conveniently prepared in good yield by adding benzoyl chloride (3 c.c.) to a solution of *N^1*-benzoylsulphanilamide (5 g.) in pryidine (50 c.c.). After ½ hour the mixture was diluted with water and acidified; the required material was then precipitated in an almost pure condition.

Sulphanilylacylamides (*N^1-Acylsulphanilamides*).—Solutions of *N^4*-acetylsulphanilamide and of the appropriate acid chloride in pyridine (5 parts) were mixed, heated on the water-bath for 1 hour, poured into water, and acidified with hydrochloric acid if necessary to complete precipitation. The precipitate was collected and refluxed in N-sodium hydroxide for 1 hour. On acidification with acetic acid the crude product was obtained.

Sulphanilylmyristamide was recrystallised from alcohol and obtained as a white crystalline product, m. p. 126° (Found : N, 7·6; S, 8·8. $C_{20}H_{34}O_3N_2S$ requires N, 7·3; S, 8·4%).

Sulphanilyladipamide, recrystallised from water, had m. p. 178° (Found : N, 9·8; S, 11·0. $C_{12}H_{16}O_5N_2S$ requires N, 9·3; S, 10·6%). Ethyl adipyl chloride was used in the preparation, the alkaline hydrolysis removing both the acetyl and the ethyl group.

Sulphanilylchaulmoogramide was prepared from chaulmoogric acid obtained by recrystallisation of high-melting fatty acids from oil of *Hydnocarpus Wightiana*. It had been hoped that some hydnocarpic acid would have been obtained, but the acylsulphanilamide obtained from these acids gave analytical results more nearly agreeing with those required for the chaulmoogryl compound. After several recrystallisations from alcohol it melted at 80—90° (Found : N, 6·45; S, 7·0. $C_{24}H_{38}O_3N_2S$ requires N, 6·45; S, 7·4%).

Dihydrosulphanilylchaulmoogramide.—Sulphanilylchaulmoogramide (10 g.) was dissolved in acetone (50 c.c.) and hydrogenated at 2 atms. by means of a charcoal–palladium catalyst. Absorption of hydrogen was rapid and ceased sharply when the theoretical quantity had been taken up. The *product*, precipitated by water, was crystallised three times from 2 parts of alcohol and then had m. p. 78—80° (Found : N, 6·3; S, 7·2. $C_{24}H_{40}O_3N_2S$ requires N, 6·4; S, 7·3%).

Disulphanilylethyleneguanidine.—Ethyleneguanidine hydrobromide (34 g.) was dissolved in 10% sodium carbonate solution (240 c.c.). To this was added slowly with shaking a solution of *p*-acetamidobenzenesul-

phonyl chloride (49 g.) in acetone (400 c.c.); the temperature rose to 30°. The precipitated solid was collected after 12 hours, and a second crop obtained from the mother-liquor by concentration. Total yield, 27 g.; m. p. 245°. The acetyl compound so obtained (32 g.) was refluxed for 1 hour with approximately 6N-hydrochloric acid (200 c.c.), and the liquid made alkaline with ammonia; the *base* (4 g.) precipitated had m. p. 178—180° (decomp.), not appreciably altered by crystallisation from 50% alcohol. The base is insoluble in alkali and therefore probably has the structure $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot N \cdot [CH_2]_2 \cdot N(SO_2 \cdot C_6H_4 \cdot NH_2)C{:}NH$ (Found: N, 16·8; S, 15·9. $C_{15}H_{17}O_4N_5S_2$ requires N, 17·7; S, 16·2%).

Sulphanilylglutamic Acid.—Glutamic acid (10 g.) was dissolved in 10% sodium hydroxide solution (100 c.c.), and *p*-acetamidobenzenesulphonyl chloride (16 g.) added slowly with shaking. After some hours the solution was acidified with hydrochloric acid and extracted with ether. The extract on evaporation left a brown residue, which was crystallised from ethyl acetate, yielding 8 g. of material, m. p. 142° (decomp.). This was hydrolysed by refluxing with 4 parts of 6N-hydrochloric acid for ½ hour. The solution was then evaporated to dryness, and the residue dissolved in a little water and neutralised with sodium acetate. Crystallisation took place; the *product* after recrystallisation from water had m. p. 192—194° (Found: N, 9·4; S, 10·8. $C_{11}H_{14}O_6N_2S$ requires N, 9·3; S, 10·6%). The *disodium* salt was obtained by adding dilute sodium hydroxide solution to an aqueous solution of the acid until it was just alkaline to phenolphthalein. The solution was concentrated and poured into alcohol, whereby the disodium salt was obtained as an amorphous precipitate, very soluble in water (Found: N, 7·9; S, 9·1; Na, 13·4. $C_{11}H_{12}O_6N_2SNa_2$ requires N, 8·1; S, 9·25; Na, 13·3%).

Sulphanilylaminoethylpyridinium Bromide.—β-Bromoethylamine hydrobromide (10 g.) was dissolved in water (90 c.c.) containing sodium carbonate (6 g.), and *p*-acetamidobenzenesulphonyl chloride (11 g.) added with stirring. After some hours the precipitate was collected, m. p. 161—164°, and refluxed for ½ hour with 6N-hydrochloric acid (100 c.c.). When the cold solution was made alkaline with ammonia, sulphanilylaminoethyl bromide was precipitated. Its solution in alcohol (7 c.c.) was diluted with an equal volume of water. The crystalline material (4·5 g.), m. p. 69—70°, thus obtained was refluxed in alcohol (15 c.c.) and pyridine (7 c.c.) for a short time. The *pyridinium bromide* crystallised on standing and after recrystallisation from alcohol (50 c.c.) and water (2 c.c.) was obtained in white crystals, very soluble in water, m. p. 218° (Found: N, 11·8; S, 8·8; Br, 22·1. $C_{13}H_{16}O_2N_3BrS$ requires N, 11·7; S, 8·9; Br, 22·3%).

4-*Benzylideneaminobenzenesulphonylglycine.*—Sulphanilylglycine was readily prepared by the Schotten–Baumann method from *p*-acetamidobenzenesulphonyl chloride and glycine. The acetyl compound which was precipitated on acidification was hydrolysed by boiling for ½ hour with 6N-hydrochloric acid. The mixture was neutralised with ammonia and made just acid to methyl-orange with dilute hydrochloric acid. The material which crystallised was recrystallised several times from water and then had m. p. 154°. A solution of it (5 g.) in hot alcohol (50 c.c.) was refluxed with benzaldehyde (2·5 c.c.) for 1 hour and then concentrated to half its bulk. After standing for several hours in the ice-box, the crystalline material was collected, m. p. 185—186° (Found: N, 9·1; S, 10·3. $C_{15}H_{14}O_4N_2S$ requires N, 8·8; S, 10·1%).

2′-*Acetoxymercuri*-3′-*hydroxybenzylidenesulphanilamide.*—Solutions of 2-acetoxymercuri-3-hydroxybenzaldehyde (5 g.) in hot acetic acid (30 c.c.) and of sulphanilamide (2·5 g.) in alcohol (50 c.c.) were mixed and refluxed, yielding yellow crystals, m. p. 282° (Found: N, 5·3; S, 6·3. $C_{15}H_{14}O_5N_2SHg$ requires N, 5·25; S, 6·0%).

8-*Quinolyl* p-*Nitrophenyl Ether.*—8-Hydroxyquinoline (44 g.) and potassium hydroxide (13·3 g.) were melted together in a three-necked flask, fitted with a stirrer and a short air-condenser, which was then placed in an oil-bath at 180°. *p*-Chloronitrobenzene (26·2 g.; 1 mol.) was added in two portions, and heating continued, with stirring, for 1½ hours. The melt was poured into 5% sodium hydroxide solution (250 c.c.) containing ice. The granular precipitate obtained was washed (55 g.), crystallised from alcohol, and distilled under 3 mm. The fraction, b. p. 285—295°, after being recrystallised from carbon disulphide, had m. p. 170°; yield, 8·4 g. It was insoluble in water and sparingly soluble in alcohol and carbon disulphide (Found: C, 68·4; H, 3·7; N, 10·5. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8; N, 10·5%).

4-p-*Nitrophenoxybenzenesulphonamide.*—*p*-Nitrodiphenyl ether (7·2 g.) was added in small portions to chlorosulphonic acid (11 c.c.; 5 mols.) at 10° with stirring. The syrup was added to ice (120 g.), and the mixture extracted with ether. The extract was shaken with 15% aqueous ammonia (14 c.c.), and the whole evaporated until a solid separated from the aqueous layer. This crystallised from alcohol in rosettes (5·4 g.), m. p. 129°, sparingly soluble in water, more freely in alcohol, readily in acetone (Found: C, 49·7; H, 3·4; N, 9·5; S, 10·7. $C_{12}H_{10}O_5N_2S$ requires C, 49·0; H, 3·4; N, 9·5; S, 10·9%).

p-*Nitrophenoxybenzenedisulphonamide* was obtained when the chlorosulphonic acid solution (previous paragraph) was heated at 95° for 2 hours and then worked up in the same way, the yield, in this case, being small. The disulphonamide crystallised from methyl alcohol in stout prisms, m. p. 270°, insoluble in water, sparingly soluble in ethyl alcohol, more soluble in methyl alcohol (Found: C, 39·1; H, 3·2; N, 11·2; S, 17·1. $C_{12}H_{11}O_7N_3S_2$ requires C, 38·6; H, 3·0; N, 11·3; S, 17·1%).

4 : 4′-*Bis*-(p-*nitrobenzamido*)*diphenylsulphone.*—4 : 4′-Diaminodiphenylsulphone (2·5 g.), dissolved in dry pyridine (4 c.c.), was treated with *p*-nitrobenzoyl chloride (3·7 g.). The *product* was recrystallised from pyridine, forming minute needles (3 g.), m. p. 346°, insoluble in water, alcohol, acetic acid or dioxan (Found: C, 57·0; H, 3·4; N, 10·3; S, 5·8. $C_{26}H_{18}O_8N_4S$ requires C, 57·2; H, 3·3; N, 10·3; S, 5·9%).

2-*Pyrrolidone*-5-*carboxy*-m-*toluidide*.—*d*-Glutamic acid (19·6 g.) and *m*-toluidine (69·8 c.c.) were heated for 24 hours at 160—170°, approximately the calculated quantity of water distilling. The excess of *m*-toluidine was removed by steam-distillation, and the solid residue crystallised from alcohol, forming thin colourless plates (17 g.), m. p. 147° (Found: C, 66·0; H, 6·3; N, 12·8. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·5; N, 12·8%).

2-*Pyrrolidone*-5-*carboxyamino*-3′-*methylbenzene*-x-*sulphonamide*.—2-Pyrrolidone-5-carboxy-*m*-toluidide (10·9 g.) was added in portions to chlorosulphonic acid (19·4 c.c.; 5 mols.), cooled by water, and the syrup heated at 50—60° for 3 hours. On pouring on ice, a solid was obtained which quickly became friable; it was washed with ice-water, treated with concentrated aqueous ammonia (7 c.c.), and kept for 1 hour. The *product*, thrice crystallised from water, formed aggregates of small plates (4 g.), m. p. 222° (Found: C, 48·9; H, 5·0; N, 14·1 S, 10·8. $C_{12}H_{15}O_4N_3S$ requires C, 48·5; H, 5·1; N, 14·1; S, 10·8%).

2-*Pyrrolidone*-5-*carboxy*-α-*naphthalide*.—An intimate mixture of *d*-glutamic acid (25·2 g.) and α-naphthylamine (115·2 g.) was heated at 185—190° for 3 hours, cooled, and triturated with ether. The insoluble residue, crystallised from alcohol, had m. p. 207°; yield, 19·2 g. (Found: C, 70·9; H, 5·5; N, 11·0. $C_{15}H_{14}O_2N_2$ requires C, 70·9; H, 5·6; N, 11·0%).

In another experiment, after additional heating for 8 hours at 210°, an *isomer* was obtained, less soluble in alcohol, and crystallising in silky needles, m. p. 224° (Found: C, 71·0; H, 5·4; N, 11·4%).

Attempts to convert these two substances into the sulphonyl chlorides were unsuccessful.

2-*Pyrrolidone*-5-*carboxy*-p-*nitroanilide*.—*d*-Glutamic acid (25 g.) and *p*-nitroaniline (111 g.) were heated together at 160° for 5 hours. The cooled melt was ground with water, dried, and extracted with ether to remove the excess of base. The residue crystallised from alcohol in clusters of yellow plates (15·6 g.), m. p. 225°, sparingly soluble in boiling water, more readily in alcohol and easily in acetic acid (Found: C, 53·3; H, 4·5; N, 16·7. $C_{11}H_{11}O_4N_3$ requires C, 53·0; H, 4·5; N, 16·9%).

2-(2′-*Pyrrolidone*-5′-*carboxy*-4″-*aminobenzenesulphonamido*)*pyridine*.—Chlorosulphonic acid (5·2 c.c.), cooled in running water, was treated gradually with *l*-2-pyrrolidone-5-carboxyanilide (3 g.), and the mixture heated at 60—70° for 3 hours, cooled, and poured on ice. The solid was twice drained on tile for ½ hour and ground with ice-water and then dried in a vacuum at room temperature [m. p. 173° (decomp.)] and added to a solution of 2-aminopyridine (1·6 g.; 2 mols.) in dry dioxan (6·4 c.c.). This mixture was heated at 95° for 15 minutes, and the upper layer poured off, leaving a viscous syrup, which was obtained crystalline by treatment with boiling alcohol. After recrystallisation from 50% alcohol the *substance* had m. p. 273°; it was very sparingly soluble in water or alcohol. Yield, 0·9 g. (Found: C, 53·2; H, 4·5; N, 15·1; S, 8·8. $C_{16}H_{16}O_4N_4S$ requires C, 53·3; H, 4·5; N, 15·6; S, 8·9%).

Diphenylsulphone-4 : 4′-*bisazo*-β-*naphthol*.—A solution of 4 : 4′-diaminodiphenylsulphone (4·61 g.) in warm 17% hydrochloric acid (92 c.c.) was rapidly cooled to − 7°, diazotised, and coupled with a solution of β-naphthol (5·75 g.) in 12·5% aqueous sodium hydroxide (154 c.c.). The scarlet *dye* was washed with hot water and alcohol; it had m. p. 304° and was very sparingly soluble in the ordinary organic solvents. Yield, 7·6 g. (Found: C, 68·5; H, 4·1; N, 9·6; S, 5·7. $C_{32}H_{22}O_4N_4S$ requires C, 68·8; H, 4·0; N, 10·0; S, 5·7%).

2 : 2′-*Dipyridyl Sulphide Dihydrobromide*.—This was prepared by the method given by Kolmer, Brown, and Raiziss (*J. Pharm. Exper. Ther.*, 1937, **61**, 256), and the m. p. and complete analysis are now recorded; m. p. 274° (Found: C, 34·4; H, 2·9; N, 8·0; S, 9·0; Br, 45·5. $C_{10}H_{10}N_2Br_2S$ requires C, 34·3; H, 2·9; N, 8·0; S, 9·2; Br, 45·6%).

2 : 2′-*Dipyridylsulphone*.—2 : 2′-Dipyridyl sulphide dihydrobromide (1 g.), dissolved in a warm mixture of acetic acid (15 c.c.) and water (3 c.c.), was treated at 50° with potassium dichromate (1·4 g.) dissolved in concentrated sulphuric acid (11 c.c.) and water (15·4 c.c.). After 1½ hours the mixture was cooled in ice and poured into water. After some hours the *sulphone* crystallised (0·42 g.), m. p. 216°. It was soluble in water and acetone, but sparingly in alcohol (Found: C, 54·7; H, 3·7; N, 13·0; S, 14·1. $C_{10}H_8O_2N_2S$ requires C, 54·5; H, 3·7; N, 12·7; S, 14·6%).

N⁴-*Quininoylsulphanilamide*.—Quininic acid (4·3 g.) was heated at 100° for 1 hour with thionyl chloride (28 c.c.), the excess of the latter removed in a vacuum at 40°, and the residue heated with a solution of sulphanilamide (3·7 g.) in dry pyridine (11 c.c.) at 110° for 1 hour. The syrup was stirred with water, and the resulting solid crystallised from alcohol. It formed nodules (3·8 g.), m. p. 255°, sparingly soluble in water (Found: C, 54·3; H, 4·7; N, 11·2; S, 8·5. $C_{17}H_{15}O_4N_3S,H_2O$ requires C, 54·4; H, 4·6; N, 11·2; S, 8·5%). This *substance* was also obtained by treatment of quininanilide with chlorosulphonic acid, and of the resulting sulphonyl chloride with ammonia.

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*-x-*sulphonamide*.—Antipyrine (10 g.) was added to chlorosulphonic acid (19·4 c.c.), cooled to − 15°. When the vigorous reaction had moderated, the mixture was heated at 90° for 1½ hours, cooled, and poured on ice. The resulting solid was treated with concentrated aqueous ammonia (8 c.c.); the product crystallised from water in stout rectangular tablets (3·6 g.), m. p. 239° (Found: C, 49·5; H, 4·8; N, 15·7; S, 12·0. $C_{11}H_{13}O_3N_3S$ requires C, 49·4; H, 4·9; N, 15·7; S, 12·0%).

In an attempt to obtain the corresponding sulphinic acid, oxidation appeared to take place with the production of the sulphonic acid (Found for the *sodium* salt: Na, 7·9. $C_{11}H_{11}O_4N_3SNa$ requires Na, 7·7%).

N⁴-*Dihydrochaulmoogrylsulphanilamide*.—Dihydrochaulmoogric acid (5 g.) was heated at 90° with purified thionyl chloride (30 c.c.) for 2½ hours and the product was freed from the excess of thionyl chloride in a vacuum at 35° and heated on the steam-bath with a solution of sulphanilamide (3 g.) in dry pyridine (9 c.c.) for 2 hours.

The resulting syrup was poured into water (250 c.c.), and the solid collected and washed (7·1 g., m. p. 178—193°). This was warmed with benzene (150 c.c.), the liquid extract centrifuged off and rejected, the paste shaken with acetone (120 c.c.) and again centrifuged. The supernatant solution was now treated with an equal volume of ether, shaken with charcoal (5 g.), and allowed to stand. The charcoal was filtered off, dried, and extracted with alcohol, which yielded the *amide* in clusters of colourless crystals, m. p. 208°, sparingly soluble in alcohol, benzene, and light petroleum, more soluble in acetone (Found: C, 66·1; H, 9·2; N, 6·4; S, 7·1. $C_{24}H_{40}O_3N_2S$ requires C, 66·0; H, 9·2; N, 6·4; S, 7·3%).

Diphenylsulphone-4 : 4′-bisazosalicylic Acid.—4 : 4′-Diaminodiphenylsulphone (5 g.), suspended in concentrated hydrochloric acid (12 c.c.) and water (24 c.c.), was diazotised in an ice-bath, and the turbid solution added to sodium salicylate (6·4 g.), disssolved in 25% sodium hydroxide solution (20 c.c.). Treatment of the clear, dark red solution with carbon dioxide precipitated a sodium salt, which formed a clear gel when suspended in 20 parts of water. This was acidified with dilute hydrochloric acid, and the precipitated solid washed with water, before and after being dried, until the washings were free from acid; m. p. 316° (decomp.) (Found: C, 57·4; H, 3·5; N, 10·0; S, 5·8. $C_{26}H_{18}O_8N_4S$ requires C, 57·1; H, 3·3; N, 10·2; S, 5·7%).

Sodium 2-Aminopyridine-N-methylenebisulphite.—29 C.c. of an aqueous solution of sodium bisulphite containing 10·6 g. were treated at 80° with formalin (7 c.c.), and 2-aminopyridine (9·6 g.) in small portions with mechanical stirring. After being kept at this temperature for 1 hour, the solution was allowed to stand overnight; it then deposited 11·2 g. of well-formed compact plates, which were recrystallised from 2 parts of hot water. The *sodium* salt had m. p. 282° (decomp.). It was readily soluble in water and very sparingly soluble in alcohol (Found: loss at 105°, 11·6; Na, for the dried substance, 10·9. $C_6H_7O_3N_2SNa,1\frac{1}{2}H_2O$ requires H_2O, 11·4%. $C_6H_7O_3N_2SNa$ requires Na, 10·94%).

Ethyl p-*Nitrobenzenesulphinate.*—Absolute ethyl alcohol (15 c.c.) containing hydrazine hydrate (3·9 c.c.) was slowly run into an ice-cooled solution of crude *p*-nitrobenzenesulphinyl chloride (obtained from 6·3 g. of *p*-nitrobenzenesulphinic acid; B.P. 509,804) in dry ether (80 c.c.). The red-brown precipitate which remained after standing for ½ hour was removed, and the filtrate evaporated to small volume; on cooling, pale yellow crystals (3·4 g.) were deposited, m. p. 48—49°. Recrystallisation from ether–light petroleum yielded long, pale yellow rhombs, m. p. 49—51° (Found: C, 45·0; H, 4·3; N, 6·4; S, 15·0. $C_8H_9O_4NS$ requires C, 44·65; H, 4·2; N, 6·5; S, 14·9%). The *ester* was readily hydrolysed to *p*-nitrobenzenesulphinic acid by aqueous-alcoholic sodium hydroxide solution.

The corresponding *methyl* ester, obtained by interaction of the acid chloride in pyridine solution with methyl alcohol, and recrystallised from ether–light petroleum, had m. p. 47° (Found: C, 42·0; H, 3·4; N, 6·8; S, 16·0. $C_7H_7O_4NS$ requires C, 41·8; H, 3·5; N, 7·0; S, 15·9%).

p-*Nitrobenzenesulphenamide.*—A dry ethereal solution of crude *p*-nitrobenzenesulphenyl chloride (9 g.) (Zincke and Lenhardt, *Annalen*, 1913, **400**, 13) was slowly run into an ice-cooled dry ethereal solution of ammonia. After ½ hour, water was added to dissolve the precipitated ammonium chloride, the ethereal solution dried over sodium sulphate, and the ether removed. The bright yellow solid residue was extracted with cold ethyl alcohol (200 c.c.), the insoluble 4 : 4′-dinitrodiphenyl disulphide filtered off, and water added to precipitate yellow crystals (4·2 g.), m. p. 101—103° (Found: C, 42·9; H, 3·6; N, 16·0; S, 18·6. $C_6H_6O_2N_2S$ requires C, 42·3; H, 3·6; N, 16·5; S, 18·8%).

4-*Nitrobenzenesulphon-4′-nitroanilide.*—*p*-Nitroaniline (0·7 g.) was added to a solution of *p*-nitrobenzenesulphonyl chloride (1·1 g.) in pyridine (1·5 g.) and heated for 2 hours on the water-bath. After cooling, the yellow mass was ground with dilute hydrochloric acid; the insoluble portion crystallised from alcohol in yellow needles or rhombs (1·2 g.), m. p. 171—173° (Found: C, 45·5; H, 2·95; N, 13·2; S, 9·5. $C_{12}H_9O_6N_3S$ requires C, 44·6; H, 2·8; N, 13·0; S, 9·9%).

4-(p-*Nitrobenzenesulphonamido-*)-4′-*nitrodiphenyl Sulphide.*—4-Nitro-4′-aminodiphenyl sulphide (1·2 g.) was added to a solution of *p*-nitrobenzenesulphonyl chloride (1·1 g.) in pyridine (1·2 g.) and heated for 1 hour on the water-bath. The resultant solid mass was cooled, ground with dilute hydrochloric acid, washed with water, and dried. Recrystallisation from alcohol or aqueous dioxan gave short, pale yellow needles (1·5 g.), m. p. 190° (Found: C, 50·0; H, 3·1; N, 10·2; S, 14·7. $C_{18}H_{13}O_6N_3S_2$ required C, 50·1; H, 3·0; N, 9·7; S, 14·9%).

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47. *The Formation and Structure of Some Organic Molecular Compounds.*

By Joseph Weiss.

The formation of the deeply coloured molecular compounds from quinones and nitro-compounds, on the one hand, and certain unsaturated hydrocarbons and their derivatives, on the other, is ascribed to a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon or its derivative (donor A) to the quinone or polynitro-compound (acceptor B) according to the net reaction $A + B \rightleftarrows [A]^+[B]^-$.

A brief quantum-mechanical discussion of this process is put forward, and the following points are then discussed in support of the theory: (*a*) The structure and the rate of formation of the molecular compounds. (*b*) The heats of formation. (*c*) The equilibrium in solution (and the influence of hydrostatic pressure upon it). (*d*) The colour of the molecular compounds. (*e*) The crystal structure and intermolecular distances. (*f*) The dipole moment in solution. (*g*) The electrical conductivity in solution. (*h*) Their relationship to the semiquinones and other free radicals and radical ions.

Molecular compounds have long been known and have found many applications in organic chemistry, particularly in recent years. In spite of this their structure has remained somewhat obscure.

The field of even the purely organic molecular compounds is a very large one (Pfeiffer, " Organische Molekülverbindungen," Stuttgart, 1927), and we shall confine ourselves to those typical classes where the colour of the molecular compound is deeper than that of either of the two components. The first group includes compounds of benzoquinones, or substances derived from them, with aromatic hydrocarbons, amines, or phenols, the quinhydrones being the best known representatives in this group. The second large group includes molecular compounds of nitro-compounds with unsaturated hydrocarbons and their derivatives: picrates are a well-known example.

Two main ideas have been put forward to explain the structure of these molecular compounds: (i) the formation to some extent of covalent links between the two components (cf. Moore, Shepherd, and Goodall, J., 1931, 1447); (ii) the saturation of residual valencies. The latter theory, originally proposed by Pfeiffer (*op. cit.*), has recently been developed by Briegleb ("Zwischenmolekulare Kräfte and Molekülstruktur," Stuttgart, 1937), according to whom the colour and compound formation are due to electrostatic interactions between the two molecules (" polarisation aggregates "). Both these theories are difficult to reconcile with the facts. More recently, Hammick (cf. Hammick and Yule, J., 1940, 1539 and earlier papers; Hammick and Sixsmith J., 1935, 580) and Gibson and Loeffler (*J. Amer. Chem. Soc.*, 1940, **62**, 1324) have suggested a polarisation mechanism similar to an oxidation–reduction reaction for the formation of molecular compounds between aromatic amines and nitro-compounds. It will now be shown that a modification and extension of this idea to the whole group of molecular compounds explains their formation and structure in every detail.

(a) *The Structure and the Rate of Formation of the Molecular Compounds.*—(1) *The ionic bond.* The components must be held together more firmly than by dipole interaction or dispersion forces. The molecular complexes very often persist in solution, and also the colour cannot be due to the saturation of residual valencies. In every case there is a simple stoicheiometrical ratio (usually 1 : 1, sometimes 1 : 2) and this alone is strong evidence against ordinary polarisation interactions.

The first analysis of the problem was made by Werner (*Ber.*, 1909, **42**, 4324). Although he did not give any detailed theory, he recognised the significance of the nitro- and carbonyl groups in the one component (irrespective of whether this is aromatic or aliphatic) and the fundamental importance of the unsaturated nature of the second component (hydrocarbons or their amino- or hydroxy-derivatives).

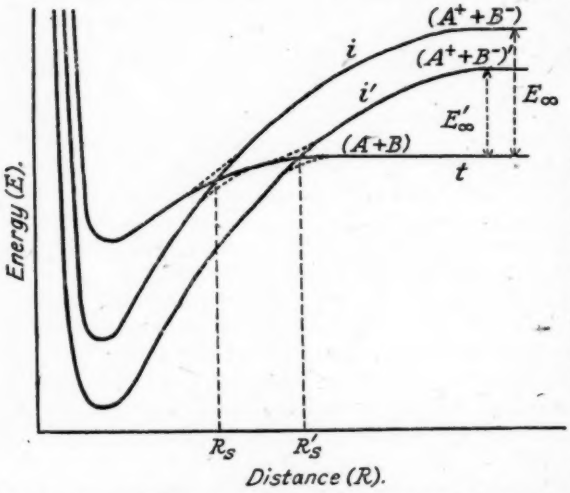
According to the author [*Nature*, 1941, **147**, 512; *Trans. Faraday Soc.*, 1941, **37**, 780 (Discussion)], the formation of the deeply coloured molecular compounds is due to a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon or its derivative (donor) to the quinone or polynitro-compound (acceptor). In general terms the donor–acceptor idea has already been put forward by other authors (*e.g.*, Bennett and Willis, J., 1929, 253; Kremann, "Ahrens Vorträge," 1924, **27**, 58), although they never proposed any detailed theory on these lines.

The acceptor molecule (B) must be one having a positive electron affinity, so it must possess one or more electronegative groups. The increase in the number of these groups favours the formation of the molecular compound through an increased electron affinity. The donor molecule (A) should have a low ionisation potential, *i.e.*, it should be capable of forming a (univalent) positive ion. The molecular compound formation is represented by the reaction

$$A + B \rightleftarrows (AB)_i \longrightarrow [A]^+[B]^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The first step is the formation of a transition complex, $(AB)_t$ (probably through dipole and dispersion interactions), and this is followed by the actual electron transfer.

The potential curves for the ionic state (i or i') and the (van der Waals) transition state (t) are schematically represented in the figure (cf. London, *Z. Physik*, 1928, **46**, 472; 1932, **74**, 143). Dispersion and dipole potentials fall off very rapidly with increasing separation R (approximately as C/R^6), and beyond a certain distance this potential is practically constant. The ionic potential (i and i') decreases more slowly [as $(I_A - E_B) - e^2/R$] for univalent ions, where I_A is the ionisation potential of the donor molecule, and E_B the electron affinity of the acceptor molecule.



Schematic representation of the potential curves for the van der Waals complex (t) and two different ionic states (i and i') corresponding to different values of E_∞ and E'_∞.

If crossing occurs at a distance (R_s) where both potentials have an appreciable value, the mutual perturbation must be taken into account, and certain linear combinations of the ionic and of the wave function derived from the van der Waals potential must be used for the description of the bond. At any rate, we will have ionic binding in the equilibrium state if the ionic state corresponds to a lower state of energy. The amount of ionic binding can be judged if one calculates the distance where the crossing occurs. If this distance is considerably greater than the intermolecular distance within the complex, the respective ionic clouds do not overlap and we have essentially an ionic bond. This distance depends largely on the value of $E_\infty (= I_A - E_B)$, small values favouring the ionic bond.

From this theory it follows that, in general, the formation will be a fairly rapid reaction, having rather a low heat of activation. This is in agreement with facts. The formation of the molecular compounds is often completely reversible without any considerable time lag. Rapid production of colour has been observed in some cases even at − 96° (Hammick, *loc. cit.*). The rate of formation of the molecular (ionic) compound is given by the following expression, which is derived on the basis of the theory of the transition complex (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; Eyring and Wynne-Jones, *J. Chem. Physics*, 1935, **3**, 107):

$$d(AB)/dt = (kT/h)K^*[A][B] \sim 2{\cdot}1 \times 10^{10}TK^*[A][B] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K^* denotes the equilibrium constant between the initial and the transition state (equation 1) and k, T, and h have their usual significance. The slow formation of certain molecular compounds, observed by Hammick (*loc. cit.*), can also be derived from equation (2) if we have reason to assume very small values for K^*.

(2) *The electron affinity of the acceptor molecule.* In the polynitro-compounds the nitro-group is responsible for the electron affinity of the molecule; consequently, this property is enhanced in, *e.g.*, tetranitromethane or *s*-trinitrobenzene. This is due to resonance between the different nitro-groups: the electron is distributed over all the groups, resulting in a decrease of its zero-point energy and an increase in the electron affinity of the molecule. A more detailed picture is the following (cf. Pauling, "The Nature of the Chemical Bond," Ithaca, N.Y., 1939; Ingold, *Chem. Reviews*, 1934, **15**, 225).

Through the inductive effect, electrons will be removed from the *o*- and *p*-positions with reference to one nitro-group, but this group can also accept an electron pair from the ring, and then we have resonance with *o*- and *p*-positions. The result of the inductive and resonance effect is that, *e.g.*, in *s*-trinitrobenzene the excess electron can resonate between all the three nitro-groups (which are in *m*-positions to each other) and the unoccupied places as well.

The formation of the picrate molecular compounds is not due to the acid character of the hydroxyl group (which manifests itself in solutions in water or other solvents of a high dielectric constant). This is shown by the fact that picric acid can form two types of compound with aromatic amines: (i) ordinary salts, formed only with strong bases, picric acid acting as an acid; (ii) true molecular compounds, formed by weak bases. These two types of compound are respectively lightly and deeply coloured. Bases of medium strength sometimes form both types, a phenomenon mainly investigated by Hertel and Schneider (*Z. physikal. Chem.*, 1930, **151**, 413; 1931, *B*, **13**, 387), who called it "complex isomerism."

The influence of other substituents on the electron affinity of the acceptor molecule can be explained in a similar way; nitro-, chloro-, and bromo-substituents increase the electron affinity, whereas the

amino-group (which through the resonance effect acts as electron repelling) and the methyl group show the opposite effect.

(3) *The ionisation potential of the donor molecule.* The only organic molecules with a low ionisation potential are those containing conjugated double bonds. The non-localised π-electrons present in these systems show a behaviour somewhat similar to that of metallic electrons. An increase in the number of conjugated double bonds reduces the ionisation potential (Price, private communication). This holds, not only for conjugated systems built up from carbon atoms, but also for those where the π-electrons come from nitrogen, oxygen, or sulphur atoms. In the donor molecule, "electron-repelling" groups as substituents, such as CH_3, OH, NH_2, NMe_2 (resonance effect through their lone pair of electrons), decrease the ionisation potential, whereas Cl and Br have the reverse effect.

(b) *Heats of Formation.*—From the theory given above, the heats of formation can be calculated in a manner similar to those of other ionic compounds. Normally, we are dealing with the molecular compound in the solid state or in solution. As the solvent effects are often very complex, we shall first consider the heat of formation in the gaseous state (ΔQ), given by the equation

$$\Delta Q = -I_A + E_B + U_C + U_P + U_D - U_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The most important contribution (after the ions have been formed) is due to the Coulombic attraction (U_C) between them. In the case of large polarisable ions or molecules, the energy due to polarisation forces (U_P) and dispersion forces (U_D) will assume greater importance. Finally, there is the term ($-U_R$) representing the repulsion potential. In the gaseous state, stable compounds should be connected with large positive values of ΔQ. The calculation of the various energy terms in equation (3) is difficult. At any rate, it would be almost impossible to compare it with the experimental values available, because all these are determined from the temperature coefficient of the light absorption in solutions of the molecular compounds (cf. Baker and Bennett, *Ann. Reports*, 1931, **28**, 137). The total heats of interaction measured in this way (ΔH) must naturally include the heats of solution of the initial products (Q_A, Q_B..) and those of the final product (Q_{AB}) in the particular solvent, as well as ΔQ itself. ΔH is given by

$$\Delta H = -Q_A - Q_B + Q_{AB} + \Delta Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the individual heats of solution involved can again be positive or negative.

Although the problem is simple in principle, the actual evaluation of equation (4) is difficult. This is why the values for the interaction energy calculated by Briegleb and Kambeitz (*Z. physikal. Chem.*, 1936, *B*, **32**, 305) are without great significance, for the solvent effects are not taken into account.

With inert solvents we often have $\Delta H > 0$, because there the first three terms in equation (4) roughly cancel each other and one measures essentially only ΔQ. In solvents containing dipole molecules (alcohol, acetone, etc.), where there are strong interactions, ΔH may be very small or even negative (Hammick, *loc. cit.*), as can be deduced from equation (4).

(c) *The Equilibrium in Solution.*—A quantitative measure of the stability of a molecular compound in solution is given by the equilibrium

$$A_{sol.} + B_{sol.} \rightleftarrows AB_{sol.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The concentration of the molecular compound in solution ($AB_{sol.}$) can be measured, for instance, by the light absorption. It is well known that an equilibrium constant for a reaction in solution ($K_{sol.}$) can be split up into a part which is independent of the solvent (K_{gas}) multiplied by the ratio of the solubilities (S_c) of the molecular species (S_A, S_B, S_{AB}) occurring in the reaction, as follows:

$$K_{sol.} = \left(\frac{[AB]}{[A][B]}\right)_{solution} = \left(\frac{[AB]}{[A][B]}\right)_{gas}\left(\frac{S_{AB}}{S_A S_B}\right) = K_g \cdot S_c \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This is derived by assuming Henry's law, *e.g.*,

$$[A]_{sol.} = S_A[A]_{gas} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The solubility of the dipole molecule (A^+B^-) should be favoured in solvents of a high dielectric constant, and this should result in a greater stability and deeper colour of the molecular compound in these solutions. However, these solvents will only be of use if the solubility of the initial products (A and B) is not too low, and if there are no specific interactions with the solvent which remove them from the equilibrium (5).

This is, *e.g.*, the case if picrates are brought into contact with water, for then the simple considerations based on the solubility and on the validity of Henry's law (7) can no longer be applied, as has been done by Dimroth and Bamberger (*Annalen*, 1924, **438**, 67). In the aqueous solution, picric acid dissociates in the ordinary way and the undissociated molecules are removed from the equilibrium (5) and transformed into picrate ions, which are not capable of acting as acceptor molecules, and consequently the molecular compound is decomposed. For the same reason alkali will decompose picrate molecular compounds even

more easily. On the other hand, hydrochloric acid decomposes molecular compounds of the amines by transforming the $R{\cdot}NH_2$ molecules into the $R{\cdot}NH_3^+$ ions.

The influence of hydrostatic pressure (II). Gibson and Loeffler (*loc. cit.*) have measured the influence of pressure on the formation of the coloured compound between nitrobenzene and aniline in a solution of 50% of each compound. Although they interpret their results in terms of reaction velocity, they have actually measured the influence of the pressure on the equilibrium corresponding to reaction (5), which is established without time lag, in a solvent mixture of the two components. The well-known thermodynamic relation can be applied to the equilibrium constant of equation (6), giving:

$$\mathrm{d}\log K_{\mathrm{sol.}}/\mathrm{d}\pi = \mathrm{d}\log K_{\mathrm{gas}}/\mathrm{d}\pi + \mathrm{d}\log S_c/\mathrm{d}\pi = -(\Delta_1 V + \Delta_2 V) = -\Delta V \quad . \quad . \quad . \quad (8)$$

$\Delta_1 V$ corresponds to the volume change of the actual association reaction in the gaseous state, and $\Delta_2 V$ to the solvent effect, *i.e.*, the influence of the pressure on the solubilities of the initial and final substances.

Gibson and Loeffler's results are somewhat contradictory at first sight because, on mixing aniline and nitrobenzene, an *increase* in volume is observed (*J. Amer. Chem. Soc.*, 1939, **61**, 2877) (ΔV positive), whereas the colour-producing equilibrium is favoured by higher hydrostatic pressure. However, it is evident from the experiments that in a solution containing 50% of each component only a very small amount of the initial products is transformed into the light-absorbing complex (probably $[PhNO_2]^-[PhNH_2]^+$). From the influence of the pressure on the light absorption, one must conclude that the coloured complex is formed with decrease in volume ($\Delta V < 0$), as is to be expected for an association reaction. This small volume decrease resulting from it must be completely superseded by another effect which occurs in the mixing of the two components (probably a change in the structure of the polar solvents) and is accompanied by an increase in volume but has nothing to do with the formation of the coloured compound.

(d) *The Colour of Molecular Compounds.*—Formation of molecular compounds is accompanied by production of a colour considerably deeper than that of the components. This also follows from the structure of such compounds as suggested above. The ions composing the compound have each an odd number of electrons, like a free radical (with a corresponding unoccupied electronic level). This gives rise to a small excitation energy and hence to light absorption in the visible. Within the ions themselves there is resonance on account of their conjugated systems of bonds, and this is accompanied by a number of polar valency structures which can contribute to the ground state and the excited state. According to Mulliken (*J. Chem. Physics*, 1939, **7**, 570 and earlier papers) this gives rise to a large transition moment and to strong absorption (charge resonance spectra).

The light absorption in a solution of the molecular compound depends on the number of ionic complexes present in the solution (*i.e.*, on the equilibrium corresponding to equation 5) and on the ionic structure of the complex. The region of absorption depends mainly on the extension of the conjugated systems of which the molecular complex is composed. Increase in the number of conjugated bonds shifts the absorption towards longer wave-lengths (cf. Foerster, *Z. Elektrochem.*, 1939, **45**, 548). All the factors which contribute towards a greater stability of the molecular compound (small value of E_∞) tend towards a deepening of the colour and an increased extinction of light. Therefore, all those substituents which decrease E_∞ deepen the colour and *vice versa*. A more direct confirmation is indicated by the fact that in the acceptor molecule the influence of substituents closely parallels their effect on the reducibility of the nitro- (or carbonyl) group (Gibson and Loeffler, *loc. cit.*, 1940). (The ease of reduction is obviously accompanied by a large value of E_B.) In the formation of the quinhydrone molecular compounds in a series of different quinones the change in the absorption spectrum brought about by the second component (forming the molecular compound) increases with increasing oxidation–reduction potential of the quinone (Hunter and Northey, *J. Physical Chem.*, 1933, **37**, 875). On the other hand the oxidation–reduction potential (of the quinone molecule and its reduced form) runs parallel to the electron affinity of the quinone. This result can be directly deduced from the above theory.

The nitro-compounds or quinone compounds of aromatic amines or phenols are more deeply coloured (more stable) than those of the hydrocarbons. The nitrogen atom has undoubtedly a greater tendency to form a positive ion than has the carbon atom. However, the binding between the aromatic amine and the acceptor molecule is not directly connected with the amino-group, as was suggested by some authors. It is again the "total" conjugated system which is responsible for the binding effect, although the resonance structures where the positive charge is on the nitrogen atom instead of on one of the carbon atoms will assume greater importance in this case. This is demonstrated by the fact that aniline and nitrobenzene give a deeply coloured compound whereas α-phenylethylamine (which is a much stronger base) does not produce any colour with nitrobenzene (Gibson and Loeffler, *loc. cit.*, 1940), because the amino-group is not directly connected to the conjugated system (and the benzene ring itself is not sufficient in this case). This view is also confirmed by the extensive work of Pfeiffer (*op. cit.*).

(e) *Crystal Structure and Intermolecular Distances.*—The crystal structure and crystallographic distances can be easily understood on the basis of the ionic character of the molecular compounds. The difference compared with simple ionic crystals (such as the alkali halides) mainly arises from the fact that in this case the ions are not spherical but are more like flat, cylindrical plates (the original molecules and the ions formed from them being essentially coplanar). Also, the ions are much larger and more polarisable, and consequently we do not usually find the simple structures as in ordinary ionic crystals. The interionic distances (3—3·5 A.) as measured by *X*-rays are of the same order as in other univalent ionic crystals (*e.g.*, potassium chloride 3·15 A., rubidium iodide 3·7 A.). In a molecular compound formed between a polycyclic hydrocarbon and, *e.g.*, picric acid, a rough estimate of the distance follows from the radius of action of the carbon atom (r_w) (cf. Schmidt, *Z. physikal. Chem.*, 1939, *B*, **42**, 83). It can be assumed that the radius of the positive ion will be somewhat smaller, and that of the negative ion presumably larger, than that of the carbon atom itself. Therefore to a first approximation the interionic distance will be of the order $\sim 2r_w \sim 3{\cdot}2$ A.

The sodium chloride type of structure has actually been observed in the system acenaphthene–2 : 6-dinitro-*m*-xylene (Hertel and Kleu, *ibid.*, 1930, *B*, **11**, 59), whereas in many other cases we find the layer lattice type (Hertel and Römer, *ibid.*, p. 77), as is to be expected with larger and polarisable ions (Hund, *Z. Physik*, 1925, **34**, 833).

(f) *The Dipole Moments of Molecular Compounds.*—According to the theory outlined above, we should expect the molecular compounds to have an electric moment due to the separation of the positive and negative charge. One should be able to measure this in the solution of the molecular compound in an inert solvent (*e.g.*, hexane). This electric moment cannot be measured in the usual way because the solubilities are too low and the molecular compound is dissociated into its components to a considerable extent. However, the existence of this dipole moment can be established in the following way. It is best to consider those molecular compounds where the polynitro-components (in virtue of their structure) must themselves have a zero dipole moment. This is the case with *s*-trinitrobenzene and *p*-dinitrobenzene, both of which have a planar configuration (Hertel and Römer, *Z. physikal. Chem.*, 1939, *B*, **22**, 267). In solvents like benzene or (molten) naphthalene these polynitro-compounds form molecular compounds (Kremann, *Monatsh.*, 1908, **29**, 863), the stability of which is favoured on account of one component being present in a high concentration. Therefore we should find a finite dipole moment for these nitro-compounds in these solvents, whereas in other solvents (which do not give rise to compound formation) the measured dipole moment will be zero. [For *s*-trinitrobenzene the non-vanishing dipole moment in benzene has already been interpreted by Bennett and Willis (*loc. cit.*) as due to the formation of a molecular compound (cf. Glasstone, " Recent Advances in Physical Chemistry," 3rd Edn., 1936, pp. 180, 181).] This is actually the case, as can be seen from the following data, in which $P_2(f_2 = 0)$ is the total molecular polarisation at infinite dilution, P_O is the orientation polarisation, and μ is the dipole moment.

	s-*Trinitrobenzene.* $[R_L]_D = 43{\cdot}5 \pm 0{\cdot}4$ c.c.[1]; $[R_L]_\infty = 41{\cdot}7 \pm 0{\cdot}4$ c.c.				*p*-*Dinitrobenzene.* $[R_L]_D = 38{\cdot}5$ c.c. (calc. from group refractions); $[R_L]_\infty = 36{\cdot}0$ c.c. (estimated).			
Solvent.	Temp.	$P_2(f_2 = 0)$, c.c.	P_O.	μ, D.	Temp.	$P_2(f_2 = 0)$, c.c.	P_O.	μ, D.
CCl_4	25°	46·6 [2]	~ 4	0 (0·2)	25°	38·9 [2]	~ 2	0 (0·1)
$CHCl_3$	25	41·3±0·5 [3]	~ 0	0	25	34·1±0·5 [3]	0	0
C_6H_6	25	55 [2]	13	0·79	25	46 [2]	~10	0·69
$C_{10}H_8$	85	55·5 [4]	13·5	0·88	—	—	—	—
$C_4H_8O_2$	25	61·5 [2]	19·5	0·96	25	47 [2]	~11	0·73

[1] Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **27**, 11.
[2] Lefèvre and Lefèvre, J., 1935, 957.
[3] Jenkins, J., 1936, 862.
[4] Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **25**, 251.

The actual values for the dipole moments given above have only a qualitative significance : the real values for the ionic complexes are probably about 10—12 times greater (8—10 D.). For accurate calculation of these from the given data an independent knowledge of the equilibrium constant of the association equilibrium (corresponding to equation 5) in the solvents benzene or molten naphthalene would be necessary.

The equilibrium constant for the association reaction is given by

$$K = Ce^{-\Delta H/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where ΔH is the heat of reaction, and C an entropy term (to a first approximation independent of the temperature) which gives a measure of the statistical probability of the associated state. For instance, for *s*-trinitrobenzene in benzene, an equilibrium constant of 10^{-3}—10^{-4} (at 25°) would be necessary to account for a dipole moment of about 10 D. for the molecular compound (as compared to the experi-

mentally determined overall value of about 1 D.). This is calculated on the basis that the total polarisation of the compound AB is made up additively from the (electronic) polarisations of its (non-polar) components plus the dipole moment created by the compound formation.

A value for the equilibrium constant smaller than unity is also supported by the experimental fact that the total polarisation of *s*-trinitrobenzene and of *p*-dinitrobenzene (although exceeding the electronic polarisation) is practically independent of the temperature over the range 25—45°. According to Debye's theory, the orientation polarisation is inversely proportional to the absolute temperature. An endothermic equilibrium will counterbalance this effect by means of the increased concentration of the association complexes at the higher temperature. For an equilibrium constant small compared to unity one can easily derive the equation

$$K_{T_1}/K_{T_2} = T_1/T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From this it is found that if the equilibrium in solution were endothermic with about 1—2 kg.-cals., this would be sufficient to account for the above-mentioned experimental fact.

For $\Delta H = 1$—2 kg.-cals. the exponential factor in the equilibrium constant (equation 9) is of the order 10^{-1}. This leaves for the entropy term a value of 10^{-2}—10^{-3}. The small value of this can be easily understood from the comparatively small statistical probability of the associated state caused by the complexity (and restricted orientation) of the associating particles (cf. Evans and Polanyi, *loc. cit.*).

(g) *Electrical Properties of the Molecular Compounds in Solution.*—If the ionic molecule is dissolved in a suitable ionising solvent we should obtain a conducting solution with the (coloured) ions migrating in the electric field. The ordinary ionising solvents (*e.g.*, water) cannot be used because the respective solubilities are too low and decomposition of the molecular compound takes place. However, the naphthalene–picric acid compound and the anthracene–trinitrobenzene compound give yellow solutions in liquid sulphur dioxide which show a small but measurable conductivity.* It is possible to demonstrate more clearly the (negative) acceptor ions and the (positive) donor ions in the following way.

If *s*-trinitrobenzene (Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, **35**, 1315) or dinitrobenzene is dissolved in liquid ammonia it forms an ionic molecular compound (with the ammonia as donor) which dissociates to some extent in the (excess) liquid ammonia. These solutions are deeply coloured owing to the negative $[R(NO_2)_n]^-$ ion, the anion $[NH_3]^+$ being colourless. On electrolysis, the coloured nitro-ion migrates to the anode, as shown by Garner *et al.* (Field, Garner, and Smith, J., 1925, **127**, 1227; Garner and Gillbe, J., 1928, 2889), who also found that these solutions behave like a binary electrolyte (*e.g.*, ammonium chloride) in liquid ammonia. According to our theory the interaction must be represented as

$$R(NO_2)_n + NH_3 \rightleftarrows [R(NO_2)_n,NH_3] \rightleftarrows [R(NO_2)_n]^- + [NH_3]^+ \quad . \quad . \quad . \quad . \quad (11)$$

The conductivity in liquid ammonia is proportional to the concentration of the ions (Garner *et al.*, *loc. cit.*), as deduced from their light absorption, which also follows from equation (11).

m-Dinitrobenzene gives a more stable and more deeply coloured solution than either the *o*- or the *p*-compound. This follows from the discussion in section (d). The rate of ionisation was found to be of the first order with regard to the *m*-dinitrobenzene (*idem, ibid.*), as can be deduced from equation (2).

Just as liquid ammonia can be used to demonstrate the acceptor ions, the solutions of hydrocarbons or amines in liquid sulphur dioxide demonstrate the donor ions. The positively charged anthracene ion is indicated by the experiments of Walden (*Z. physikal. Chem.*, 1903, **43**, 385), who found that even dilute solutions of this hydrocarbon in liquid sulphur dioxide are deeply yellow and show a measurable conductivity (at a concentration of 10^{-2} mol./l. the equivalent conductivity is $\Lambda \sim 0{\cdot}1\ \Omega^{-1}$ at 0°). This is due to the primarily formed compound $[C_{14}H_{10}]^+[SO_2]^-$ which is (slightly) dissociated in liquid sulphur dioxide. More basic substances such as diphenylamine, dimethylaniline, and α-picoline have a much lower ionisation potential and can form molecular compounds with sulphur dioxide more easily (cf. Foote and Fleischer, *J. Amer. Chem. Soc.*, 1934, **56**, 870). These complexes, which are soluble in liquid sulphur dioxide with a deep red or brown colour, show a considerable conductivity in this solvent (Walden, *loc. cit.*) (10^{-2} mol. of α-picoline per l. shows an equivalent conductivity of $\Lambda_\infty = 6{\cdot}63\ \Omega^{-1}$ at 0°).

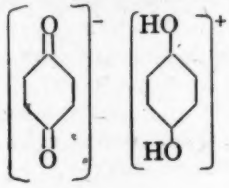
(h) *The Structure of Molecular Compounds and their Relation to the Semiquinones.*—(1) *The hydrogen bond and dismutation.* With quinones and polynitro-compounds we have the following groups of molecular compounds:

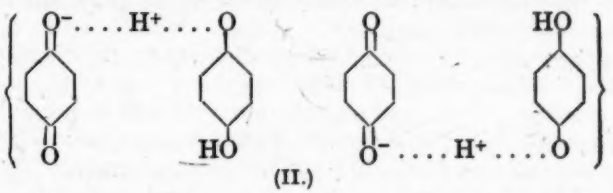
Acceptor (anion).		*Donor (cation).*
Quinones	—	Hydrocarbons Phenolic compounds Amino-compounds
Nitro-compounds		

The best-known compound in the first group is quinhydrone. Benzoquinones (*e.g.*, tetrachlorobenzoquinone) are also capable of forming deeply coloured compounds with aromatic hydrocarbons.

* Unpublished experiments (at concentrations of about 10^{-3} mol./l. the equivalent conductivity is of the order of $0{\cdot}1\ \Omega^{-1}$ at 0°).

The relationship to the semiquinones (cf. Michaelis, *Chem. Reviews*, 1935, **16**, 243) becomes apparent if we consider, for instance, the structure of quinhydrone from the point of view of our theory. Introducing the idea of the simple electron transfer, one obtains the structure (I). Generally, the positive and the negative charges are "smeared out" over the whole of the respective conjugated system. However, there is a tendency for the negative charge to stay on the oxygen of the carbonyl group and for the positive charge to concentrate on the hydroxyl groups. Actually we have the ideal conditions for a

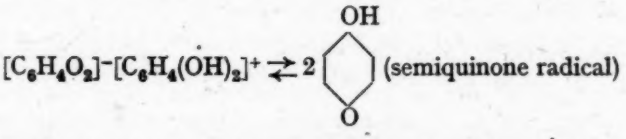
(I.) 



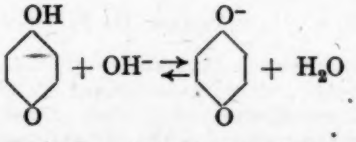
(II.)

hydrogen bond (Pauling, *op. cit.*): the proton is held between the neutral and the negatively charged oxygen. The structure of quinhydrone in the solid state and in non-ionising solvents is then represented by the resonance structures shown in (II) with hydrogen bonds. In agreement with this, the quinhydrones in the solid state are diamagnetic (Coryell, quoted by Pauling, *op. cit.*). The deep colour of these compounds (in non-ionising solvents) is not due to the formation of semiquinones (cf. Litschitz, *Ber.*, 1915, **48**, 1734; Wagner and Grunewald, *Z. Elektrochem.*, 1940, **46**, 265), but must again be attributed to the polar structure.

If the proton is *completely* transferred we get in this particular case:

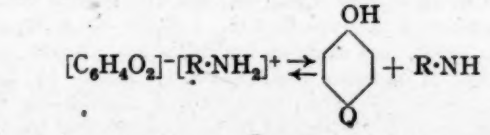


i.e., the formation of 2 molecules of semiquinone according to a dismutation equilibrium. In the solid state and in media of low dielectric constant the equilibrium is usually towards the left-hand side of the equation. In aqueous solutions and particularly in the presence of alkali the semiquinone is transformed into its ion:



This ion is rather stable because of the resonance of the electron between the oxygen atoms, and it cannot undergo dismutation on account of its negative charge (Coulombic repulsion). It has all the properties of a free radical, and the alkaline solutions of quinhydrones are therefore paramagnetic (Michaelis, Schubert, Reber, Kuck, and Granick, *J. Amer. Chem. Soc.*, 1938, **60**, 1678).

The same ideas can be applied to the molecular compounds with amines:



In this case we get two different semiquinones. The "quinhydrone" formation between phenazine and dihydrophenazine must be treated on exactly the same lines as above (Clemo and McIlwain, J., 1934, 1991).

(2) *Ions and free radicals.* We have seen that the positive ions of the phenolic compounds and amines which appear in the structure of the molecular compounds are really identical with the well-known semiquinones. The connection between them is given through the equilibria:

$$[R{\cdot}NH_2]^+ \rightleftarrows \underset{\text{(radical)}}{R{\cdot}NH} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$[R{\cdot}OH]^+ \rightleftarrows \underset{\text{(radical)}}{R{\cdot}O} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In the solution it depends entirely on the hydrogen-ion concentration whether they are present as radicals or as ions according to the reactions (12) and (13).

The same idea, when applied to conjugated hydrocarbons which behave similarly to their hydroxy- or amino-derivatives, leads to a new type of " semiquinone " which must be described as a positive hydrocarbon ion. This is in equilibrium with the free radical and hydrogen ions:

$$[C_nH_m]^+ \rightleftarrows C_nH_{m-1} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

An independent confirmation of these new types of ions can be found in the recent experiments (Weiss, *locc. cit.*) on the formation of various positive ions from conjugated systems such as anthracene, coronene, and even graphite.*

In the case of the quinhydrones the negatively charged quinones are also identical with the semiquinone. The existence of singly negatively charged polynitro-molecules is confirmed independently by the formation of a coloured negative ion in the solutions of polynitro-compounds in liquid ammonia. This is also supported by the formation of a deeply coloured compound from *s*-trinitrobenzene (and similar nitro-compounds) with metallic sodium or potassium,† the complex probably containing the same negative ion.

There are a few cases of molecular compounds where the molecular ratio is 1 : 2 instead of the usual 1 : 1 (cf. Cook and Robinson, J., 1938, 509). This is to be expected, for instance, in the comparatively rare cases in which we have two more or less separate regions of influence in the same molecule (cf. Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 144), which is then capable of forming a doubly charged positive (or negative) ion. It can also be expressed in another way, *viz.*, that the 1 : 1-molecular compound (which is in any case the primary product) must still be able to act either as an acceptor or as a donor towards one of its components. The doubly charged ions would again have an even number of electrons and should therefore be chemically more stable and less deeply coloured than the univalent ions which correspond to free radicals.

My thanks are due to Professor G. R. Clemo and Professor C. K. Ingold for their interest in this work, and particularly to Professor J. W. Cook, Professor Peierls, and Professor Polanyi for many most valuable discussions.

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48. *The Primary Gaseous Products of Carbonisation.*

By K. BOLTON, J. E. CULLINGWORTH, B. P. GHOSH, AND JOHN W. COBB.

Substances differing widely in constitution and oxygen content were subjected to fractional carbonisation up to 1100°. Liquid products were evolved up to 600°. *X*-Ray powder photographs were made of the solid residues from cellulose and glycine. These disclosed an early breakdown of the original structure, followed by a repatterning of the carbon atoms in a hexagonal graphitic network visible at 400—500°, and more distinct from 800° upwards. The specific gravities of the same residues rose rapidly up to 800°, much more slowly afterwards. The primary gaseous products were specially studied, and their formation from the solids and from simple aromatic hydrocarbons compared. In the initial decompositions the gaseous products displayed wide quantitative differences, but afterwards were fundamentally similar, being evolved in the succession methane, hydrogen, carbon monoxide, and believed to arise from ·CH_3, ·H, and ·OH groups (attached to the hexagonal network) by molecular condensations of the type $R_1{\cdot}CH_3 + R_2H \longrightarrow R_1R_2 + CH_4$. The maximum methane evolution was at 500—600°, and that of hydrogen and carbon monoxide at 700—800°. The single hexagonal carbon ring of benzene was apparently broken by rise of temperature with comparative ease, but the solid hexagonal carbon network was unbreakable by that means.

The hydroxyl group was held to form steam and become responsible for the formation of carbon monoxide as water gas by the gasification of nuclear carbon from the hexagonal network. The ideas that the free evolution of hydrogen from coal at 700—800° was (1) the property of one kind of constituent or (2) due to secondary decompositions, were both found untenable.

THE term " carbonisation " is used to denote the process of decomposition by rise of temperature which converts a carbon compound into a solid residue richer in carbon and approximating more closely to carbon itself as the temperature is higher and the time of heating more prolonged. In a typical applic-

* The polycyclic hydrocarbons are really amphoteric. We have seen that they can act as donors (forming positive ions) or as acceptors, as is well known from the compounds of naphthalene, anthracene, and phenanthrene with metallic sodium or potassium. We have found that even such highly symmetrical hydrocarbons as coronene ($C_{24}H_{12}$) can form deeply coloured compounds with these metals quite easily, where they are most probably present as negative ions.

† Unpublished results. This compound is formed by shaking the solution of the nitro-compound in ether with the finely divided alkali metal.

ation of the process to a solid, chemical breakdown begins before simple volatilisation of the substance carbonised, and proceeds by a succession of decompositions to yield solid, liquid, and gaseous products. The experimental analysis of the process demands that, as far as possible, (1) the substance shall be homogeneous, *e.g.*, a definite chemical compound, (2) the temperature shall be raised gradually and maintained at each level until the decomposition at that level is complete, and (3) the volatile products shall be removed so quickly at each temperature level from the region of decomposition that further secondary decomposition is minimised. In such an industrial process as the carbonisation of coal, no one of these conditions is even approximately satisfied, so that, although chemical and thermal studies of large-scale carbonisation, treating coals of many kinds in different ways, have been usefully made, they have not given and cannot give the data for such an analysis of the essential features of the carbonisation process as is now desired. The method of fractional carbonisation has not been followed in such large-scale experiments because it is not practicable to secure gas-tightness of the apparatus over the long periods of time necessary for even approximate completion of reaction at each of a succession of chosen temperatures, and even if that were done the size of the apparatus and charge would facilitate secondary decompositions in the primary products. Numerous laboratory investigations, particularly those of the late R. V. Wheeler and his collaborators, have amplified our information by small-scale work including some fractional and vacuum carbonisation, but they have dealt usually with coal and the lower temperature phenomena, and so have served to bring out the peculiarities and differences in a narrow range of substances rather than the resemblances which, as will be seen, emerge in a wider survey having more regard to higher temperatures. Moreover, the method of experiment followed, particularly for high temperatures, has commonly been not to fractionate but to take a number of separate charges of the substance under test to different temperatures, noting the difference in result.

This method cannot serve the purpose of a fractional carbonisation. The products from such an experiment at any temperature will be a mixture of primary products at that temperature, surviving primary products from lower temperatures, and secondary products from all the decomposed primaries. It is difficult to draw conclusions from any such experiment, and the results by two investigators will disagree unless all their conditions of operation are identical. For instance, although such work by Wheeler *et al.* (J., 1910, **97**, 1917, etc.) led them to conclude that there was a critical point in the decomposition of coal (attributed by them to its ulmin constituents) about 700°, marked by a greatly increased evolution of hydrogen, and that of Vignon (*Compt. rend.*, 1912, **153**, 1514) was confirmatory, yet Porter and Taylor (*Proc. Amer. Gas Inst.*, 1914, **9**, i, 234), on the basis of their own experiments, regarded the increased hydrogen evolution at 700—800° as due rather to secondary decomposition of tars and gases than to a breakdown of the coal substance as a whole—leaving the position in an obscurity which has not been removed (cf. Bone and Himus, " Coal : Its Constitution . . .," p. 161, 1936).

It may be reasonably expected that in carbonisation, as the temperature rises, the almost infinite variety of stable molecular constitutions and aggregations which are possible at room temperature will give place, under the stress of increasing molecular agitation, to more stable structures richer in carbon, following lines of decomposition converging to carbon itself and shedding volatile products, liquid and finally gaseous, in the process.

In the work now described, the gaseous products have been singled out for examination. The substances carbonised represented a wide range of chemical constitution and complexity. They were : cellulose, bakelite, glycine, petroleum coke, anthracite, and New Hucknall and Sharlston Wallsend coals.

Experimental.

The method of experiment was the same throughout. The substance was heated in stages of 100° in a vacuum, and the gas formed at each stage was collected, measured, and analysed. On plotting the volume of the gaseous products obtained, it was found that the emission of a particular gas was not confined to one temperature stage, but that a stage of maximum emission (or at times more than one maximum) was usually well marked, so that the succession of decompositions could be clearly traced. The ideal was to complete the gas evolution at one temperature stage before proceeding to the next, but that was not feasible, and long-continued emissions were regarded as complete when the rate fell below 1 c.c. per hour.

Apparatus.—A vitreous silica tube, as used in the Gray–King high-temperature assay of coal, rounded at one end and stoppered at the other, with a small side tube near the stoppered end projecting downward, was heated in an electrical resistance furnace. The 5 (or 10) g. charge was packed at the rounded end and lay entirely in the constant-temperature region of the furnace. Nearly all the remaining free space of the tube was filled by several vitrified Morgan fire-clay blocks; the under surface of each block but the one next to the charge was grooved, and the furnace was sloped towards the exit tube. In this way a minimum time of contact before leaving the heated tube was secured for the gases, and any liquid condensing in the cooler exit end was drained away quickly, so that secondary decompositions were prevented as far as possible. (Preliminary trials showed that with widely different rates of carbonisation only the same very thin dark

film formed on the tube.) The exit tube dipped straight into an air condenser in which liquid collected; this was followed by a bubbler containing glycerol and water or, if any ammonia was present, dilute sulphuric acid. Gas then passed to a mercury-sealed holder, and by means of a Sprengel pump the pressure was kept below 10—20 mm. of mercury, except during short periods of rapid emission.

In carrying out an experiment, the gas-tightness of the apparatus having been tested by leaving it overnight under vacuum, the temperature was raised at the rate of 100° per hour and halted at each 100° for the emission of gas at that temperature. The result reported for any temperature relates to the gas emitted in reaching that temperature from one 100° lower and in maintaining it at that temperature until emission could be regarded as complete. Some experiments occupied several weeks, and in such cases a little in-leakage of air was responsible for nitrogen and oxygen totalling, on the average, 1·6% in the gas collected, but analyses are reported " nitrogen and oxygen free " unless otherwise described. The carbonisation was usually carried up to 1200° or 1300°, but there was a liability to increased leakage at 1200°, so results are tabulated only up to 1100°, although many obtained at the higher temperatures gave no obvious reason for suspicion.

Gas analyses were carried out in the Bone and Wheeler apparatus. Unsaturated hydrocarbons were determined by absorption in a half-saturated solution of bromine in water, hydrogen and carbon monoxide by passage over copper oxide at 280° and washing with sodium hydroxide solution, and paraffins by after-combustion over copper oxide at a red heat. Any oxygen resulting from slight dissociation of the copper oxide was removed by washing with alkaline pyrogallol after absorption of the carbon dioxide resulting from the combustion.

Results.—These are presented in the tables, which give the volumes of gas (in c.c. at N.T.P.) evolved per g. of substance carbonised, and are illustrated in the figure.

Cellulose, $(C_6H_{10}O_5)_n$.—Whatman filter-paper clippings were used. Previous work had paid more special attention to liquid and solid products. Lebeau carried out a fractional carbonisation at 100° intervals but for only one hour at each temperature, so his results, although generally similar to ours, are only roughly comparable.

Progress of carbonisation on 10 *g. up to* 1100°. Total time, 1199 hrs.; 860 hrs. from 700° upwards. Maxima of gas emission at 300° and 800° (rapid emission noted at 280°). Heavy evolution of reddish-brown liquid at 300°. No liquid products above 600°. Of 0·49 g. of oxygen in 1 g. of cellulose, 0·10 g. was evolved as carbon monoxide and 0·09 g. as dioxide, *i.e.*, 39% as oxides of carbon. The gas evolved in the first 24 hrs. at 1100° contained H, 59·7; CO, 40·3%; and that in the remaining 238 hours H, 52·3; CO, 47·7%. The approach to water gas is noteworthy (see Discussion below).

Cellulose, $(C_6H_{10}O_5)_n$.

	Temperature.									Total up to 1100°.	Vol. %.
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.		
CO_2	38·0	11·5	4·2	1·9	2·2	2·4	0·2	—	—	60·4	15·2
C_nH_m (unsatd.) ...	0·9	1·2	0·3	—	—	—	—	—	—	2·4	0·6
H_2	0·1	0·9	6·4	17·6	27·7	36·6	29·2	28·0	19·7	166·2	41·9
CO.....	17·4	15·9	10·0	5·4	8·9	22·6	22·0	22·4	16·8	141·4	35·5
C_nH_{2n+2}	0·4	6·5	8·9	6·5	2·9	0·8	0·2	—	—	26·2	6·8
Total.....	56·8	36·0	29·8	31·4	41·7	62·4	51·6	50·4	36·5	396·6	100·0
Value of n in C_nH_{2n+2}.....	1·5	1·3	1·1	1·0	1·0	1·0	1·0				

Solid residues. Those used for a specific-gravity determination and *X*-ray examination were obtained as follows: For that at any one temperature $t°$, cellulose was heated at 100° per hour to $t - 100°$, held at that temperature for 24 hours, heated to $t°$ in one hour, and held at $t°$ for 24 hours. Prolonged exposure was thus secured, and gas samples drawn at each temperature, compared with those from the fractional carbonisation, indicated the same reactions, but volumes were somewhat smaller. The specific gravity results obtained were:

Temp.	15°.	200°.	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1200°.
d	1·60	1·61	1·41	1·38	1·42	1·59	1·70	1·82	1·82	1·86	1·86	1·85

The rapid increase between 600° and 800° and the slow increase afterwards are notable.

Bakelite.—The sample used, presented by British Bakelite Ltd., was a light yellow, powdered resin with a strong phenolic odour; it was described as prepared from a mixture of phenol and formaldehyde, with ammonia as catalyst. On gentle heating it did not fuse but gave some liquid with the odour of phenol. (The special property of formaldehyde resin is that it polymerises on heating, hardens and becomes very insoluble.) In ultimate analysis it resembled a coal, rich in hydrogen and oxygen.

Progress of carbonisation on 5 *g. up to* 1000°. Total time, 785 hrs.; 662 hrs. from 700° upwards. Maximum gas emission at 800°. First analysed gas emission, very slow and in small volume, at 400°. Liquid products in some quantity at 100° and 200°, none above 600°. 1 G. of bakelite as carbonised contained 0·162 g. of oxygen, of which 0·105 g. was evolved as carbon monoxide and 0·010 g. as dioxide, *i.e.*, 71% as oxides of carbon. Fractional analysis was made of gas evolved in periods at the higher temperatures:

	In rise 700—800°.	First 30 mins. at 800°.	Remainder at 800°.	Similar remainder at 1000°.
H_2, %	77·9	82·8	58·3	58·1
CO, %	18·0	15·2	40·2	40·9
CO_2, %	3·3	1·5	0·2	0·2
CH_4, %	0·8	0·5	1·3	0·8

Results from the other samples corresponded.

Bakelite.

	Temperature.							Total up to 1000°.	Vol. %.
	400°.	500°.	600°.	700°.	800°.	900°.	1000°.		
CO_2	0·4	0·8	1·3	3·3	0·8	0·3	0·2	7·1	1·4
C_nH_m	0·1	0·3	0·4	—	—	—	—	0·8	0·2
CO	0·5	4·8	11·7	14·8	40·6	38·1	36·7	147·2	28·5
H_2	1·0	17·8	57·3	63·6	71·5	59·9	54·0	325·1	62·9
C_nH_{2n+2}	1·1	11·6	17·4	3·0	1·4	1·2	0·7	36·4	7·0
Total	3·1	35·3	88·1	84·7	114·3	99·5	91·6	516·6	100·0
Value of n in C_nH_{2n+2}	1·4	1·0	1·0	1·0	1·0	1·0	1·0		

In another fractional carbonisation of bakelite, the time at any one temperature stage was limited to 24 hours. The same reactions were indicated, but the volumes of hydrogen and carbon monoxide collected from 700° upwards were roughly halved.

Glycine.—Progress of carbonisation on 5 *g. up to* 1100°. Time, 951 hrs.; 665 hrs. from 700° upwards. Initial gas evolution noted at 245°, maxima collected at 300° and 800°. Slight smell of cyanogen. Mist at 200°, liquid from 300° to 500° and possibly 600°. 1 G. of glycine contained 0·43 g. of oxygen of which 0·07 g. was evolved as carbon monoxide and 0·12 g. as dioxide, *i.e.*, 44% as oxides of carbon.

Glycine, $NH_2{\cdot}CH_2{\cdot}CO_2H$.

	Temperature.									Total up to 1100°.	Vol. %.
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.		
CO_2	41·4	28·9	5·3	1·8	1·9	2·2	1·0	0·2	0·1	82·8	24·0
C_nH_m	0·3	0·3	0·3	0·1	0·0	—	—	—	—	1·0	0·3
CO	1·8	5·6	8·9	6·2	10·0	17·3	14·6	16·3	16·0	96·7	28·0
H_2	0·1	0·4	5·3	16·8	23·9	30·5	23·1	17·7	16·6	134·4	38·0
C_nH_{2n+2}	0·5	0·5	7·2	4·1	1·8	1·1	0·2	0·1	0·1	15·6	4·5
N_2	—	0·1	0·5	0·5	1·2	3·1	4·3	2·9	1·9	14·5	4·2
Total	44·1	35·8	27·5	29·5	38·8	54·2	43·2	37·2	34·7	345·0	100·0
Value of n in C_nH_{2n+2}	1·1	1·1	1·1	1·0	1·0	1·0	1·0	1·0	1·0		

The close approximation to water gas in the composition of the 1100° fraction is again noteworthy (cf. Cellulose).

Yields of ammonia. Ammonia was not determined in these experiments but of 0·187 g. of nitrogen contained in the glycine 0·018 g. (by diff.) was evolved as free nitrogen. In a fractional carbonisation made by A. C. Monkhouse (1922, Leeds, unpublished), rather less than 50% of the nitrogen of glycine was obtained as ammonia up to 600° and a further 38% between 600° and 1000°, of which 12% was free nitrogen, 7·4% remaining in the coke. In another of our fractional carbonisations of glycine carried to 1300°, 19·6% of coke was obtained containing 3·64% of nitrogen, *i.e.*, 3·8% of the original nitrogen. It was evident that ammonia had been evolved in stages, the partial evolution at any one temperature being accompanied by the formation of a solid residue which evolved no more ammonia or nitrogen at that temperature but decomposed further at a higher temperature. There was no one temperature characteristic of ammonia evolution. Previously reported work on the thermal decomposition of glycine had been carried out at low temperatures and indicated dehydration, fusion without decomposition, and decarboxylation as primary results (*e.g.*, Balbiano, *Ber.*, 1900, 33, 2324).

Petroleum Coke.—This was supplied by the Anglo-Iranian Oil Co. and resulted, according to Dr. A. E. Dunstan, " from the cracking of distillate oils at pressures round about 650/750 lbs. and at temperatures round about 450°." The coke contained some oils and, before use in the fractional carbonisation, was extracted with ether, then with carbon disulphide, and again with ether, any solvent being finally driven off by heating at 105° in an air-oven. It then contained C, 94·7; H, 3·3%.

Progress of carbonisation of 5 *g. up to* 1100°. Time, 72 hrs.; 50 hrs. from 700° upwards. Gas evolved negligible below 500°. This substance displayed peculiarities in the carbonisation, probably connected with the high pressure of preparation. The first small gas fraction was collected at 500° and contained nearly all the carbon dioxide evolved in the carbonisation and some nitrogen and oxygen. In another experiment, when this fraction was collected in two equal portions, the whole of the nitrogen and free oxygen were found in the first portion. These were presumably derived from air adsorbed under the high pressure of preparation, but the proportions, 25·2 and 2·5%, respectively, suggested that some of the oxygen had gone into combination. The liberation of gas generally was slow, and that of methane more widespread in temperature than with the

other substances carbonised, showing a maximum at 700°. Evolution of hydrogen was still incomplete at 1300°, and a much more prolonged carbonisation would probably have been justified.

The outstanding feature of the carbonisation was the pronounced increase in evolution of hydrogen from 700° onwards. In this respect the behaviour of petroleum coke was the same as that of cellulose and all the other materials carbonised. The only rapid evolution of gas with petroleum coke occurred during the first hour at 700° and 800°.

Petroleum coke.

	Temperature.							Total up to	Vol.
	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1100°.	%.
CO_2	2·2	0·2	—	—	—	0·1	—	2·5	1·5
C_nH_m	0·4	0·2	1·0	0·6	0·4	0·1	0·0	2·7	1·6
CO	1·2	0·3	0·6	—	—	0·7	0·5	3·3	2·0
H_2	5·5	12·7	42·9	29·2	27·5	10·7	7·9	136·4	81·7
C_nH_{2n+2}	3·1	4·0	6·9	5·5	1·8	0·4	0·4	22·1	13·2
Total	*12·4	17·4	51·4	35·3	29·7	12·0	8·8	167·0	100·0
Value of n in C_nH_{2n+2}	1·2	1·1	1·0	1·0	1·0	1·0	1·0		

* Also N_2, 1·7; O_2, 0·2%.

Anthracite.—This contained O_2, 2·0; H_2, 3·2%.

Progress of carbonisation to 1100°. Time, 63 hrs.; 46 hrs. from 700° upwards. First decomposition noted at 500° as shown by evolution of gas and also of a small quantity of liquid which was noticeable up to 600°. Gas evolution rapid at beginning of each heating at 700—1100°, and slow evolution continued at 1200—1300°. The volume of hydrogen emitted rose rapidly at 700° and continued large at 800° and 900°. Most of the small oxygen content appeared as carbon monoxide, suggesting previous molecular condensation (see Discussion); of 0·020 g. of oxygen contained in 1 g., 0·013 g. was evolved as this oxide and 0·005 g. as dioxide, *i.e.*, 90% as oxides of carbon.

Anthracite.

	Temperature.								Total up to	Vol.
	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1100°.	%.
CO_2		0·7	1·0	1·3	0·2	0·2	0·1	0·1	3·6	1·4
C_nH_m		0·0	0·3	—	—	—	—	—	0·3	0·1
CO		0·4	1·6	5·7	4·4	2·4	2·4	2·0	18·9	7·4
H_2		1·2	17·5	66·0	50·5	41·6	13·2	12·7	202·7	79·4
C_nH_{2n+2}		2·0	13·0	7·6	3·5	1·4	0·4	0·3	28·2	11·0
N_2 (diff.)		0·0	0·1	—	0·2	1·1	0·1	0·2	1·7	0·7
Total	(0·4)	4·3	33·5	80·6	58·8	46·7	16·2	15·3	255·4	100·0
Value of n in C_nH_{2n+2}		1·0	1·0	1·0	1·0	1·0	1·0	1·0		

Of the products, 88·9% were solid, 7·6% gaseous, and (by diff.) 3·5% liquid.

New Hucknall Coal.—This was a bituminous, fusible, coking coal containing C, 77·4; H, 5·6; S, 1·6; N, 1·3; ash, 3·8; O (by diff.), 10·3%.

Progress of carbonisation to 1100°. Time, 78 hrs.; 40 hrs. from 700° upwards. First decomposition (gas and trace of tar) noted at 400°. Rapid gas evolution first noted at beginning of heating at 500° (methane at maximum), then again at 700° (hydrogen at maximum) onwards. Slow evolution continued at 1200° and 1300°. Of 0·103 g. of oxygen contained in 1 g. of coal, 0·055 g. was evolved as carbon dioxide and 0·023 as dioxide, *i.e.*, 76% as oxides of carbon.

New Hucknall coal.

	Temperature.								Total up to	Vol.
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1100°.	%.
CO_2		1·8	1·9	1·6	4·3	2·8	2·8	0·4	0·1	15·7	4·0
C_nH_m		0·2	1·0	0·5	1·1	—	—	—	—	2·8	0·7
CO		1·1	6·2	5·4	11·5	13·7	19·9	11·2	8·3	77·3	19·6
H_2		0·1	6·2	17·3	57·2	49·9	41·9	26·3	17·9	216·8	54·8
C_nH_{2n+2}		4·1	29·6	16·2	12·8	5·8	1·9	0·5	0·3	71·2	18·0
N_2 (diff.)		0·1	0·4	0·3	2·5	3·1	2·1	1·6	1·4	11·5	2·9
Total	(1·4)	7·4	45·3	41·3	89·4	75·3	68·6	40·0	28·0	395·3	100·0
Value of n in C_nH_{2n+2}		1·7	1·4	1·1	1·1	1·0	1·0	1·0	1·0		

Of the products, 61·5% were solid, 21·4% gaseous, and (by diff.) 17·1% liquid. In a much more rapid carbonisation (2¾ hours) of 30 lbs. of this coal (moisture, 5·0%) to 976° on a semi-commercial scale in a horizontal cronite retort on the Corbet–Woodall experimental plant at the University of Leeds, the results were: coke, 65·5; gas, 17·6; tar and pitch, 6·1; liquor, 10·7%. The gas contained much more unsaturated hydrocarbons, 4·9%, and much less carbon monoxide, 11·3%, than in our fractional carbonisation where the high carbon monoxide resulted from a slow and long-continued reaction and the volatile matter was not subjected to decomposing influences.

Sharlston Wallsend Coal.—This was also carbonised, for comparison; it contained C, 82·9; H, 5·4; S, 0·9; N, 1·3; ash, 0·9; O (by diff.), 8·6%. Like New Hucknall coal, it was a fusible, bituminous, coking coal and the results of the carbonisation, being very similar, are not reported. There was, however, one striking difference. Of 0·086 g. of oxygen contained in 1 g. of coal, 0·011 g. was evolved as carbon monoxide and 0·006 as dioxide. Thus, although this coal contained nearly as much oxygen as the New Hucknall, only about one-fifth as much was evolved as oxides of carbon. The explanation lies presumably in the greater molecular condensation which the New Hucknall coal had already undergone in formation, so that, on heating, a much larger proportion of the oxygen was left in the form of firmly attached hydroxyl groups surviving to react with hydrogen and carbon (see Discussion) in the higher temperature range to produce carbon monoxide. Bakelite had disclosed the same phenomenon.

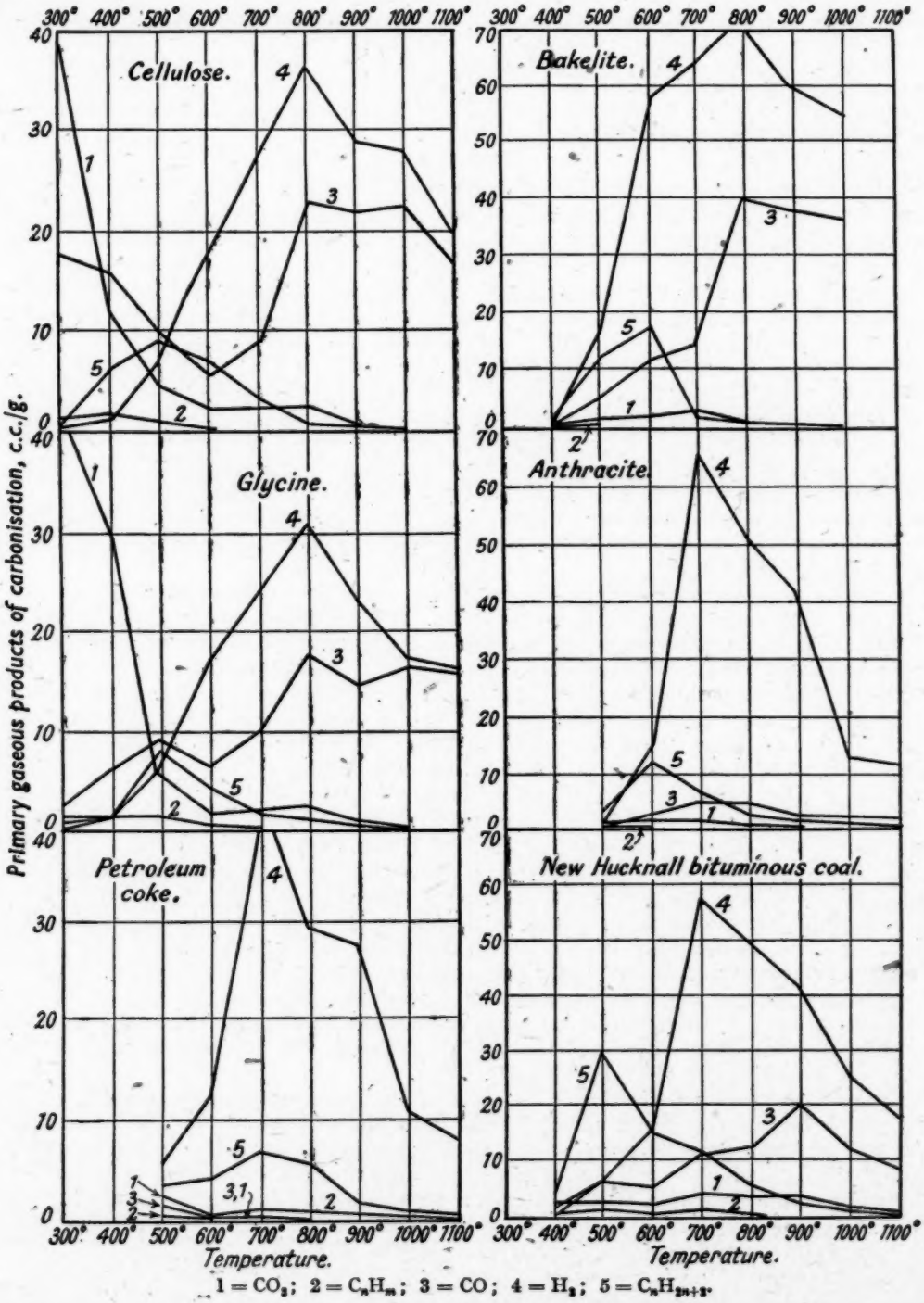
Discussion.

A striking feature of the results detailed above and displayed in the tables and the figure is the general similarity in the nature and temperature sequence of the primary gaseous products of decomposition from substances of widely different composition and complexity. In every case the decomposition occurred in two phases. In the first, lasting up to 600°, the gaseous products were accompanied by liquids which were not examined but obviously varied widely and by their removal were largely responsible for the progress towards a common type of solid residue; in the gaseous products methane was prominent in every case, with a maximum emission at 500—600°. In the second phase, from 700° upwards, there were no liquid products but always a dominating emission of hydrogen, accompanied by widely differing quantities of carbon monoxide, both persisting at the highest temperatures of these experiments although in greatly diminished quantity. In the first phase, the emission of gas at each temperature could be completed (*i.e.*, reduced to <1 c.c./hr.) in a reasonable time of heating. In the second phase, the emission of hydrogen (and carbon monoxide) increased rapidly at 700°, and although it fell away to a slow rate on continued heating at that temperature, its cessation could at times not be secured even after many days. The same was experienced on raising the temperature further to 800°, so that the choice between 700° and 800° as the temperature of maximum emission was somewhat arbitrary.

X-Ray Evidence.—The gas emission may be considered in relation to the changes in the solid residues disclosed by an *X*-ray examination made for us by Dr. W. T. Astbury and Dr. E. Green (Ph.D. Thesis, Leeds, 1938). Cellulose residues from 200° to 1200° at 100° intervals, and glycine residues at 400° and 1200° were examined. Below 200° cellulose showed no change, but at 300° the rings in the *X*-ray photograph of unheated cellulose had given place to a general diffuseness, which indicated a break-down of the original structure. Some aromatisation has been detected chemically below this temperature (Smith and Howard, *J. Amer. Chem. Soc.*, 1937, **59**, 234). At 400° a carbon re-patterning was already in evidence, and at 500° the appearance of the two most characteristic rings as given by graphite denoted the formation of a hexagonal network of carbon atoms in parallel sheets. The rings were somewhat diffuse at this stage, such as would be given by very minute or imperfectly formed crystals, and the diffuseness persisted at higher temperatures. At 800° it was greatly lessened, but even at 1200° was still there. The sharpness of the rings shown on a comparison photograph from graphite was lacking. Moreover, as observed by others, at the first appearance of the carbon network the spacing between the sheets was slightly larger than in graphite. Although much more extensive surveys on crystallite growths during carbonisation have been made by Riley and others with similar results, yet it was desirable for our purpose to demonstrate by this examination what had occurred to the solid residues in their prolonged heating when decomposition had reached approximate finality at the successive stages of temperature. A carbonisation rate of 5°/min., with 10 mins. at the final temperature, had been found by Blayden, Riley, and Taylor to provide sufficient time for maximum crystallite growth (*J. Amer. Chem. Soc.*, 1940, **62**, 180; J., 1939, 67).

Perhaps the most striking indications were those of the lower-temperature residues, *viz.*, that the disruption of the original compound under thermal shock, in evidence at 300°, had been followed so quickly at 400° and 500° by rearrangement of carbon atoms in a hexagonal network so fundamentally resistant that the increasing thermal shocks of higher temperatures only resulted in its further growth and stabilisation. The formation of such a carbon network would be effected no doubt in different ways according to the constitution of the original compound decomposed. Thus the fusion of glycine at a low temperature would confer a much greater degree of molecular mobility and facilitate the rearrangement of carbon atoms in the new and more stable formation. In some other substances, such as the coals, the existence of six-membered carbon rings in some quantity at the outset, as demonstrated chemically by Fischer and Schrader, Francis and Wheeler, and more convincingly and quantitatively by Bone *et al.* (*Proc. Roy. Soc.*, 1927, *A*, **110**, 537, etc.), would assist in providing nuclear centres for the growth of the carbon network, again facilitated if the coal were fusible. But the progress in every case examined is towards an ultimate residue of graphitic carbon by the splitting away of a variety of larger

molecular groups, up to 600°, which volatilised and condensed to liquids on cooling, and of gases in an orderly succession up to the highest temperature used in the fractional carbonisation. This succession has been our special study.



Primary Gaseous Products.—These were principally methane, hydrogen, and oxygen in the form of the two oxides of carbon. *Methane and hydrogen.* These may be considered together. The maximum methane emission was at 500—600°, above which it fell away rapidly and was replaced by an extensive hydrogen emission, at a maximum from 700° to 800°, falling away slowly at first, then more rapidly to

the highest temperatures used. A useful comparison can be made with the break-down of simple aromatic hydrocarbons. It was found (Dufton and Cobb, *Trans. Inst. Gas Eng.*, 1919, 137) that benzene, with nitrogen as a neutral carrier gas, underwent its first decomposition at 650° with the (reversible) formation of a single condensation product, diphenyl, and hydrogen: $2C_6H_6 \longrightarrow (C_6H_5)_2 + H_2$. At 750° the decomposition was much more extensive, with the formation of more condensation products, including diphenylbenzene and hydrogen and also, significantly, some methane, the carbon of which could only come from the incipient breakdown of the benzene nucleus. The first decomposition of toluene in nitrogen was also a condensation at nearly the same temperature (600°) as for benzene, with emission of hydrogen complicated almost at once by the formation of methane from the methyl group and of benzene. Here again the amount of condensation products, hydrogen and methane, obtained at 750° indicated rapid extension of the decomposition with the rise to that temperature. Similar experiments carried out by F. J. Dent and assistants in this laboratory [see 41st Report of the Joint Research Committee of the Institution of Gas Engineers and the University of Leeds (*Trans. Inst. Gas Eng.*, 1937)] were confirmatory and were extended to coals, coke, and lignite, with special reference to the influence of pressure and atmosphere on the formation of methane. From a comparison of the results obtained with xylene and with benzene, heated in hydrogen at 50 atm. pressure, it was deduced that in the production of methane from xylene, commencing slowly at 500° and quickening rapidly up to 800°, the methane below 675° came from " a hydrogenation of the side chains which was sensibly complete at 700°," but the rest of the methane came from nuclear carbon. With low-temperature cokes, prepared at 400—450° and heated in hydrogen under pressure, however, the rate of production of methane passed through two distinct maxima, one at 500—550° and the other at 750—800°, and it was suggested that " the first maximum was due to the hydrogenation of side chains, chain compounds, etc., and the second was caused by the hydrogenation of the basic six-membered carbon rings." With heating in nitrogen at normal atmospheric pressure, the first methane maximum was fully in evidence, although less pronounced than with high-pressure hydrogen, but the second was absent, being replaced by a hydrogen maximum in the same temperature range, 750—800°. Other fuels gave similar results.

Comparison of the behaviour of simple aromatic hydrocarbons and of the substances used in our experiments discloses interesting resemblances and differences. In the first place, the temperature, 700—800°, which brought about marked molecular condensation and consequent emission of hydrogen with benzene, toluene, and xylene, was also that of maximum hydrogen emission in all the solid substances carbonised; *i.e.*, the specific reaction $2C_6H_6 \longrightarrow (C_6H_5)_2 + H_2$, involving two single six-membered rings, and a generalised reaction $R_1H + R_2H \longrightarrow R_1R_2 + H_2$ in the solid hexagonal network of carbon atoms formed in the carbonisation, both became prominent at 700—800°. The *X*-ray phenomena provided evidence of this changing solid structure, as did also the changes in specific gravity during carbonisation: that of the carbonised cellulose increased rapidly in the process from 1·42 in the 500° to 1·82 in the 800° residue, but much more slowly afterwards (see p. 254). Similar results for specific gravity had been obtained from a bituminous coal and anthracite by Greenwood and Cobb (*J. Soc. Chem. Ind.*, 1922, **41**, 181; Lane, Leeds Thesis, 1934) and from Durham bituminous coals by Drakeley and Wilkins (*ibid.*, 1931, **50**, 331). A diminution in the electrical resistance of powdered coke from 1,000,000 units when prepared at 650° to 180 when prepared at 750°, noted in " The Solid Products of the Carbonisation of Coal " (South Metropolitan Gas Co., 1934, p. 59), is another striking indication of radical change effected in the solid structure when a temperature of 750° has been attained in carbonisation.

With methane, however, the temperature range of maximum emission from the solid substances carbonised was no longer the same as from the simple aromatic hydrocarbons, but distinctly lower. With toluene it was practically the same as the range of maximum hydrogen emission, and with xylene the formation of methane by hydrogenation under pressure appeared to be continuous for the attached groups and the nuclear carbon, but with the solid substances carbonised the maximum decomposition producing methane occurred in a lower temperature range (500—600°) than that producing hydrogen (700—800°), and there were two corresponding methane maxima on hydrogenation under pressure. The growth of the hexagonal carbon network in the solids, indicated by the *X*-ray examination of cellulose and glycine as occurring at temperatures well below that of the main condensation producing maximum hydrogen may well be the mark of more easily effected condensations of the type $R_1{\cdot}CH_3 + R_2H \longrightarrow R_1R_2 + CH_4$ coming into play at these lower temperatures. There was plainly little survival of attached methyl groups to the higher temperature range in the substances carbonised, except with petroleum coke, from which the emission of methane was apparently more widely spread, perhaps as a consequence of this material having been prepared under high pressure (650—750 lbs./in.^{2}).

Apart from the condensations just considered, there are, of course, the varied decompositions and

aromatisation from which a little methane and other gaseous hydrocarbons appeared from the beginning of breakdown, but it is clear that in all the substances carbonised the emission of methane at 500—600° was outstanding. The value of n in the paraffins C_nH_{2n+2} was usually 1·0; it exceeded 1·1 only for the small volumes of the initial decompositions and for the bituminous coal up to 600°; the highest value obtained was 1·7 for the small yield of gas (7·4 c.c. per g.) from the bituminous coal at 400°.

There is an important respect in which the decomposition of the solids differs from that of benzene. At 750° benzene decomposes with the production of methane in a quantity increasing with further rise in temperature, but the solids in carbonisation, after the free emission at 500—600°, yield only small and diminishing volumes of methane unless treated with hydrogen under pressure. This phenomenon seems to demand the interpretation that the single hexagonal carbon ring of benzene can be broken by rise of temperature with comparative ease, but that the solid hexagonal carbon network is unbreakable by that means. It forms the "fixed carbon" of a proximate analysis. This increased resistance conferred by consolidation of the benzene ring structure has other manifestations. Carbonised residues from anthracite, bituminous coal, lignite, peat, wood, and cellulose have been shown to be much less active with sulphuric acid when the temperature of preparation reaches 700—800° (South Metropolitan Gas Co., *op. cit.*, p. 40). This is the region of extensive molecular condensation marked by maximum hydrogen emission on heating and rapid increase in specific gravity. Similarly, in Bone's work, the benzenecarboxylic acids formed by the attack of permanganate on carbonised residues increased with the temperature of carbonisation until that had reached 600°, but then diminished, which surely meant, not that the six-membered carbon rings were diminishing in number, but that their aggregations were becoming more resistant. How far the increase in stability can go with rise in temperature and increasing consolidation of structure is seen in an extreme case from an extension of Dent's experiments on the hydrogenation under pressure of carbonised residues, to crystalline graphite, which was found to be completely inert. (Of course the degree of consolidation represented by crystalline graphite with its specific gravity of 2·25 is much greater than that attained in our experiments or in commercial carbonisation, where the maximum specific gravity reached may be taken as 1·9.)

Hydrogen was the most voluminous primary gaseous product of decomposition. In our experiments, the first gas samples collected in quantity allowing of analysis always contained a little hydrogen. As the temperature rose, the volume of hydrogen increased, more rapidly from 500° upwards, until the maximum was reached at 700—800°, after which it fell away, but the emission was never complete at 1100°. From 700° upwards, our practice of collecting gas at any one temperature until its rate of emission had fallen below 1 c.c./hr. (see p. 253) could not always be followed without an impracticable extension of the time of carbonisation, which, as it was, reached 860, 662, and 665 hrs. from 700° upwards with cellulose, bakelite, and glycine respectively. At 700° gas came away rapidly at first but, after a time, at a slow rate falling almost imperceptibly. The same occurred at 800°, and the choice between 700° and 800° as the temperature of maximum emission became rather arbitrary. This slow-continuing emission of gas was probably due partly to its location between superimposed planes of the solid hexagonal network which were closing up to form graphitic crystallites, a phenomenon studied by Riley and others (*e.g.*, J., 1936, 456).

There was, however, another even more potent cause of the continuing slow emission of gas at these higher temperatures, *viz.*, the greatly enhanced production of carbon monoxide, which began at the same temperature as that of hydrogen, 700° or a little higher. Moreover, with the more highly oxygenated substances such as cellulose and glycine, and higher temperatures, the gas evolved approximated more and more closely in composition to ideal water gas (equal vols. of hydrogen and carbon monoxide), and the same tendency displayed itself unmistakably with other substances if the gas at any one temperature was collected fractionally. For instance, with bakelite, although the gas evolved in the first ½ hour at 800° contained 82·8% of hydrogen and 15·2% of monoxide, the remainder contained 58·3 and 40·2% respectively (with small quantities of carbon dioxide and methane). In no case, however prolonged the heating, did the gas sample contain more carbon monoxide than hydrogen. It seems that, from 700° upwards, two reactions occur side by side; at each temperature a rapid generation of hydrogen is prominent early, whereas the slower generation of water gas tends to predominate later. This continuing emission of carbon monoxide in coal carbonisation was noted by Burgess and Wheeler (J., 1911, **99**, 661), who suggested the action on carbon "of any steam formed" as the cause. That supposition is fully justified by our results. Exactly what happens is not deducible with certainty, but a hypothesis consistent with the facts is that the formation of carbon monoxide (as water gas) is analogous in its mechanism to that already put forward for hydrogen and methane, and that it depends upon the formation of steam by a molecular condensation which can be most simply represented as $R_1{\cdot}OH + R_2H \longrightarrow R_1R_2 + H_2O$, the steam so liberated then attacking the carbon. Nuclear carbon of the hexagonal network would be so attacked, and indeed only a small quantity

of any other carbon survives to that temperature range. According to Rau and Lambris (*J. Gasbel.*, 1913, **56**, 561), on gradual heating of cellulose 600° was the highest temperature at which water was evolved, and coals behaved similarly. Above that temperature presumably any steam formed would combine with carbon. Surviving hydroxyl groups attached to the hexagonal network would provide steam in the manner suggested, and the formation of water gas would proceed from 700° upwards as indicated in our experiments.

The high-temperature evolution of oxygen in combination with carbon as carbon monoxide just considered followed, with every substance, upon a low-temperature evolution, mainly as carbon dioxide. The two stages were most plainly exhibited by glycine and cellulose, from which oxygen as carbon dioxide, along with much smaller quantities of carbon monoxide, came away quickly at 300°, diminished greatly in the medium range of temperature, and was finally evolved again in quantity as carbon monoxide from 700° upwards. With bakelite and anthracite, the low-temperature emission of oxides of carbon was negligible in comparison with that occurring from 700° upwards. For this, antecedent molecular condensations in the preparation of the bakelite and in the natural formation of the anthracite may be regarded as responsible. Determinable quantities first appeared at 400° for bakelite and 500° for anthracite. The two bituminous coals differed in behaviour though not much in oxygen content, New Hucknall (with 10·3% of oxygen) resembling bakelite in its much larger emission of carbon monoxide at high temperatures. Both coals gave only small emissions of oxides of carbon at low temperatures, commencing at 300—400°. Again a difference in antecedent molecular condensations during formation may be held responsible, leading to a greater survival of firmly attached hydroxyl groups above 700° with the New Hucknall coal.

Attention may be directed to the complex results in the very gradual process of fractional carbonisation arising from the single carboxyl group of glycine (the only possible source of oxides of carbon), results strikingly similar to those obtained from the much more complex cellulose. Another example is forthcoming in the behaviour of the single amino-group of glycine, which was found responsible in fractional carbonisation for the emission of ammonia in temperature stages and for nitrogen held in the solid residue (see above). It is plainly not permissible to connect complexity (or simplicity) of behaviour on heating with that of original constitution—a not unnecessary warning. It is always to be remembered that the gaseous products of carbonisation are not emitted from the original substance but from the solid residue as existing at the temperature of emission, and that residues from different substances have so far conformed to a common type after the first few hundred degrees of carbonisation that the composition of the gaseous products offers only a limited guidance to the original constitution.

Unsaturated hydrocarbons (C_nH_m). These formed a very small proportion of the gaseous products in fractional carbonisations but they appeared in the first analysable volume forthcoming from each substance and their emission sometimes persisted up to 600°. The volumes obtained ranged from 0·3 and 0·8 c.c./g. for anthracite and bakelite to 2·8 c.c./g. from the two bituminous coals—well under 1% of the gas in every case. (A commercial carbonisation of these coals would have given about 4% in the gas.) In laboratory carbonisations of 20 g. of Sharlston Wallsend coal up to 800° at 5°/min., in apparatus generally resembling the one we used, N. R. Balmford (Leeds, Thesis, 1934) obtained gas containing 1·6% of unsaturated hydrocarbons, but when all the volatile products were passed through a short length of tube, maintained throughout at 800°, the percentage was raised to 4·5 as a result of the secondary decomposition thereby effected. The tar yield was correspondingly diminished. Moreover, it was found by Jones and Wheeler (J., 1914, **105**, 141, 2562, etc.) that oils boiling below 300°, distilled from the tar obtained by the vacuum distillation of a bituminous coal at 430°, contained 40—45% of "ethylenic" unsaturated compounds, and Jones reported later (J., 1915, **107**, 1106) that heating the vaporised tar at temperatures from 550° to 800° decomposed naphthenes, paraffins, and unsaturated hydrocarbons present in it, to form olefins which condensed at higher temperatures to form aromatic substances. Thus, the low yield of unsaturated hydrocarbons in our fractional carbonisation of bituminous coals is not surprising, and the same explanation presumably holds for the other substances carbonised, *viz.*, that the "ethylenic" groups when present were largely retained in the liquid products. To establish this firmly throughout would, however, require an examination of these products.

Ammonia. This was not determined in these fractional carbonisations, but in previous work carried out on Sharlston Wallsend and a second bituminous coal and on anthracite, by carbonising them in a current of nitrogen, and keeping them for an hour at each temperature interval of 100° up to 1000°, it had been noted that the maximum ammonia emission had in each case occurred at 700—800°, *i.e.*, at the same temperature as the accompanying maximum hydrogen emission in the same experiments (Eastwood and Cobb, *Trans. Inst. Gas Eng.*, 1931, 272). The parallel was so close as to suggest a similar mechanism of reaction, as was then pointed out, such as $R_1{\cdot}NH_2 + R_2H \longrightarrow R_1R_2 + NH_3$, the amino-group being expelled with accompanying molecular condensation. Similar results were obtained

from glycine carbonised in the same way by another observer (J. E. Knight), although in that case there was a previous free emission of ammonia and carbon dioxide at 400°.

It is of interest that the bituminous coals, which in normal commercial or laboratory carbonisation fused and formed firm cokes, were only slightly coherent powders after the fractional carbonisation of our experiments. It would appear that the molecular groups responsible for fusion and the cementing of particles in normal carbonisation, had been expelled in the much slower heating, before a temperature had been reached at which they could exercise this influence. No such complication occurred with glycine, which fused completely before decomposition and yielded a firm, shrunken, porous coke on further heating.

Conclusions.

The fractional carbonisation of a solid, in the light of the foregoing experimental results and discussion, may be viewed thus: The first stage is a destruction, more or less complete, of the original molecular and crystalline pattern by the enhanced internal vibrations brought into play by the rise in temperature. With many substances, *such as form a solid residue on carbonisation*, there follows a repatterning of carbon atoms in a hexagonal network which is such a stable arrangement that it can resist any disintegrating tendency of further temperature rise and forms graphitic crystallites. *X*-Ray methods applied by Dr. W. T. Astbury showed this repatterning established at 400—500°. Its progress was accompanied by an increase in specific gravity, rapid up to 800°, much slower afterwards up to 1200°. (In such material as coal some of the carbon is in the hexagonal pattern from the beginning.) Meanwhile, other molecular groups form no part of the new stable hexagonal pattern, or are easily detached from it, and with the rise of temperature these are volatilised or decomposed, each being expelled at once, if volatile, at the temperature of its formation, or otherwise when its temperature of volatilisation has been reached. Some of these are the liquid products of carbonisation, and their expulsion, beginning early, continues up to about 600°. They are characteristic of the substance undergoing carbonisation, and by their loss the various residues assume a similarity of constitution. Some gaseous products appear early. Carbon dioxide, with some monoxide, is evolved in quantity even at 300° from such highly oxygenated substances as cellulose and glycine, with small volumes of hydrogen and paraffins and unsaturated hydrocarbons. With substances relatively poor in oxygen which have already undergone some molecular condensation, naturally or artificially, the first samples analysed in our experiments contained in small volume these same gases emitted at rather higher temperatures, 400° for coal and bakelite, 500° for anthracite and low-temperature petroleum coke. This first emission of gas in small volume may well arise largely from secondary decomposition of the larger molecules of liquid products, marking a failure to realise completely in practice the ideal fractional carbonisation. In several previous investigations of fuel, directed more especially to the initial products of decomposition, water and the oxides of carbon have been shown to be the first to leave. Our procedure with 100° intervals did not detect this.

Then follows the emission in all cases of the chief primary gaseous products, methane, hydrogen, and carbon monoxide. They may be regarded as coming from the more firmly attached $\cdot CH_3$, $\cdot H$, and $\cdot OH$ groups by molecular condensations, of the type exemplified by $R_1H + CH_3R_2 \longrightarrow R_1R_2 + CH_4$, in the growing and consolidating hexagonal network. The maximum methane emission is at 500—600° and that of hydrogen and carbon monoxide at 700—800°. (The maximum ammonia production from coals at 700—800° in other experiments was probably derived similarly from attached amino-groups.) The hydroxyl group, by forming steam, becomes, on this view, responsible for the formation of carbon monoxide as water gas by the gasification of nuclear carbon from the hexagonal network. The evolution of carbon monoxide and hydrogen together seems to proceed more slowly than the direct condensation yielding hydrogen, with the result that the gas expelled at the higher temperatures from a substance rich in oxygen, and particularly that part of the gas collected after long heating at one temperature, approximates to ideal water gas in composition.

The methane has some admixture of higher paraffins, but it is slight, as indicated by the value of n in C_nH_{2n+2}, and most noticeable in the small volumes emitted at the beginning of carbonisation. Unsaturated hydrocarbons are produced to a very limited extent—well below 1% in the substances tested. The differences between the gaseous products of fractional and commercial carbonisation come from the overlapping of stages and incompleteness of reactions in the latter, and to a large extent from the decomposition of primary liquid products.

The experimental work described above brings out the fundamental similarity in the primary gaseous products of fractional carbonisation from a number of substances differing widely in chemical constitution, particularly when the stage of initial decomposition has been passed. With special reference to coal the results confirm Burgess and Wheeler's conclusion that there is a critical temperature of decomposition in its carbonisation, marked by greatly enhanced evolution of hydrogen, at 700—800°,

and lend no support to Porter and Taylor's contention that this phenomenon is due to secondary decomposition. They indicate clearly, however, that this is not a special property of coal, and still less of any one of its petrographical constituents. The greatly enhanced evolution of hydrogen (and carbon monoxide) at 700—800° is apparently a normal feature of molecular condensation in solid residues formed at lower temperatures in the carbonisation.

We thank the firms mentioned above for the provision of samples, Mr. H. J. Hodsman for advice and assistance throughout in the experimental work, and Dr. W. T. Astbury for the *X*-ray examination of carbonised residues.

FUEL DEPARTMENT, THE UNIVERSITY, LEEDS. [*Received, January 7th*, 1942.]

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49. *Compounds of Naphthoic Acids with their Copper and Nickel Salts. Copper and Nickel Sulphinates and their Oxidation to Sulphonates.*

By (MRS.) W. G. WRIGHT.

Copper and nickel salts of α- and β-naphthoic and α- and β-naphthalene- and *p*-toluene-sulphinic acids are described. The naphthoic acids form both acid and basic compounds, but the sulphinic acids form only normal salts. With the exception of nickel α-naphthalenesulphinate, the compounds of the α-acids are soluble in organic solvents, and those of the β-acids insoluble. In this respect they resemble the acid potassium compounds.

The oxidation of the sulphinates to the corresponding sulphonates is described, and the dehydration of the sulphonates is discussed.

A crystalline basic compound of copper β-naphthoate is described.

COPPER and *nickel α-naphthoate* and *copper α-naphthalenesulphinate* are all soluble in organic solvents, whereas the corresponding *salts* of the β-acids are insoluble. In this respect they resemble the α- and β-acid potassium compounds, the former having the properties of an un-ionised compound, and the latter those of a salt (Wright, J., 1940, 859). It is notable, however, that all the copper salts have the strong green colour characteristic of co-ordinated copper, suggesting that this difference is not one of degree of ionisation. Since it exists in the copper compounds as well as in the acid potassium compounds, the difference in the latter case cannot be connected with the acidic hydrogen; *i.e.*, it is not due to the two molecules being connected, the α- by the potassium atom, causing chelation, and the β- by the hydrogen atom, leaving the potassium ionised.

With β-naphthoic acid, copper and nickel form both basic and acid *compounds*: β-$Cu(C_{10}H_7\cdot CO_2)_2,Cu(OH)_2$; 3β-$Cu(C_{10}H_7\cdot CO_2)_2,C_{10}H_7\cdot CO_2H$; 3β-$Ni(C_{10}H_7\cdot CO_2)_2,Ni(OH)_2$; β-$Ni(C_{10}H_7\cdot CO_2)_2,C_{10}H_7\cdot CO_2H,2H_2O$. With α-naphthoic acid, copper forms a basic and nickel an acidic *compound*: α-$Cu(C_{10}H_7\cdot CO_2)_2,Cu(OH)_2$; α-$Ni(C_{10}H_7\cdot CO_2)_2,C_{10}H_7\cdot CO_2H,2H_2O$. The acid salts of the β-acid are both formed by the action of acetone on the normal salt, the basic compounds being simultaneously precipitated. Basic nickel β-naphthoate is also formed by the action of other organic solvents on the normal salt, β-naphthoic acid being produced in solution. Basic copper β-naphthoate is soluble in aqueous ammonia and is deposited in deep blue prisms as the ammonia evaporates on exposure to air. Crystalline copper hydroxide has been prepared in this manner (Hayek, *Monatsh.*, 1936, **67**, 352).

The acid nickel salts of both α- and β-naphthoic acids melt at comparatively low temperatures. Both the hydrates and the dehydrated substances are soluble in organic solvents.

Copper and nickel sulphinates do not form either basic or acid compounds. The copper salts are characterised by a bright yellow colour which changes to green on hydration but is not regenerated when the hydrates are dried at 100°, the latter retaining their green colour and crystalline appearance.

Copper α-naphthalenesulphinate is highly hydrated. It slowly dissolves in cold water to form a pale blue solution, from which bright yellow, anhydrous flakes separate on heating, and very pale blue, almost colourless prisms of a hexahydrate separate at 0°. In this substance the brilliant colour of co-ordinated copper is markedly absent, and it seems likely that the copper ion is completely surrounded by water molecules. The hexahydrate loses all its water at 45°, becoming bright yellow. It is insoluble in organic solvents, but in contact with acetone or chloroform the crystals turn into the bright yellow anhydrous substance, and then dissolve, forming yellow solutions. In benzene the crystals remain unchanged and insoluble.

Separation of α- and β-Naphthoic Acids.—The solubility of the copper salt of the α-acid and the insolubility of that of the β-acid in alcohol provide a convenient method of separating the two acids when prepared from the mixed product of the sulphonation of naphthalene.

Identification of α- and β-Naphthalenesulphinic Acids.—The copper salts of both α- and β-naphthalenesulphinic acid are precipitated by adding copper nitrate to neutral solutions of the ammonium salts. As the β-compound is bright yellow when precipitated, and rapidly turns green on the filter, whereas the α-compound is precipitated as the almost white hexahydrate, this constitutes a method of distinguishing between the two acids, whose m. p.'s, 96° and 98°, are too near for identification purposes.

Oxidation of Sulphinates to Sulphonates in Alcoholic Solution.—The *p*-toluenesulphinates are readily oxidised to the corresponding sulphonates in alcohol. The bright yellow alcoholic solution of copper *p*-toluenesulphinate is immediately decolorised on evaporation in air, becoming strongly acid; the solution yields only crystals of the sulphonate. The nickel salt is oxidised when a current of air is passed through its suspension in boiling alcohol; after some hours a clear green solution is produced, which yields crystals of the pure *sulphonate*, no other substance being formed.

Copper β-naphthalenesulphinate is only partly oxidised to sulphonate by the latter process; other acid copper substances are produced, some copper oxide is precipitated, and a bright yellow oil formed. On addition of benzene to the concentrated alcoholic solution, however, a 50% yield of the sulphonate separates. Similar results are obtained with the nickel compound. Copper α-naphthalenesulphonate cannot be obtained from the sulphinate by this method, but the nickel sulphonate is formed so readily that it is the sole product of the action of nickel carbonate on α-naphthalenesulphinic acid in alcoholic solution, and constitutes about 50% of the product when the reaction takes place in ether.

Dehydration of Sulphonates—As the extensive hydration of the sulphonates has been discussed in connection with the maximum co-ordination number of copper, it is noteworthy that copper and nickel *p*-toluenesulphonate and copper β-naphthalenesulphonate lose only $4H_2O$ at 100°, falling into white powders. Since the acids themselves are monohydrates, the other two molecules of water are probably attached one to each acid radical. Moreover, α-naphthalenesulphonic acid, which is a dihydrate and cannot be dehydrated without decomposition (Fierz and Weissenbach, *Helv. Chim. Acta*, 1920, **3**, 314), yields a copper salt which loses only $2H_2O$ at 100°.

Experimental.

Copper *p*-toluenesulphinate was described by Meyer (*J. pr. Chem.*, 1901, **63**, 171) as a pale green trihydrate. By the action of copper carbonate on *p*-toluenesulphinic acid in alcoholic solution, however, it was obtained as a yellow precipitate; this was sparingly soluble in boiling water, grass-green plates of the trihydrate separating from the boiling solution [Found: Cu, 14·7; loss at 100°, 12·7. Calc. for $Cu(C_7H_7{\cdot}SO_2)_2,3H_2O$: Cu, 14·9; $3H_2O$, 12·6%]. Pale green needles, also of the trihydrate (Found: Cu, 14·7; loss at 100°, 12·44%), separated from the cooled solution at 40°, and dark green needles of the *hemihydrate* separated from the cold solution on standing overnight [Found: C, 44·0; H, 4·1; Cu, 17·0; loss at 100°, 3·3. $Cu(C_7H_7{\cdot}SO_2)_2,\frac{1}{2}H_2O$ requires C, 43·9; H, 3·9; Cu, 16·6; $\frac{1}{2}H_2O$, 3·1%].

Copper *p*-toluenesulphonate and copper and nickel α- and β-naphthalenesulphonates have been described (*Ber.*, 1879, **12**, 1851; Fierz and Weissenbach, *loc. cit.*; Witt, *Ber.*, 1915, **48**, 755), but only for copper β-naphthalenesulphonate has the loss of water at lower temperatures than those required for complete dehydration been noted. Witt describes a loss of 4 mols. at 75—80°, and Fierz and Weissenbach only 2 mols. at 80°. The sulphonates prepared by oxidation of the sulphinates, and also from the sulphonic acids for verification, gave the following results: copper *p*-toluenesulphonate hexahydrate lost $4H_2O$ at 100°, forming a white powder (Found: loss, 14·06. Calc. for $4H_2O$: loss, 14·0%); on complete dehydration a green powder was produced (Found: loss at 240°, 20·9. Calc. for $6H_2O$: loss, 21·0%). Copper β-naphthalenesulphonate hexahydrate lost $4H_2O$ at 100°, falling into a white powder (Found: loss, 12·36. Calc. for $4H_2O$: loss, 12·3%). Nickel β-naphthalenesulphonate suffered no loss in weight at 100°. Copper α-naphthalenesulphonate hexahydrate lost $2H_2O$ at 100°, its crystalline appearance remaining unchanged, but its colour fading (Found: loss, 6·23. Calc. for $2H_2O$: loss, 6·14%); on complete dehydration the colour became bright orange, but the crystalline structure was undamaged (Found: loss at 185°, 18·2. Calc. for $6H_2O$: loss, 18·4%). Nickel α-naphthalenesulphonate hexahydrate lost $3H_2O$ at 100° and $4H_2O$ at 150°, and was completely dehydrated at 185°, its crystalline appearance remaining unchanged (Found: loss at 100°, 150°, and 185°, 9·3, 12·5, 18·9 respectively. Calc. for 3, 4, and $6H_2O$: loss, 9·3, 12·3, 18·6%, respectively).

Nickel Salts of Naphthoic Acids.—*Nickel α-naphthoate* was formed as a pale green precipitate by the action of nickel carbonate (0·75 g.) on α-naphthoic acid (3 g.) in alcohol (15 c.c.), some remaining in the alcohol. It crystallised from boiling water as a tetrahydrate in pale green prisms, soluble and stable in alcohol, acetone, ether, chloroform, and benzene [Found: Ni, 12·2; loss at 100°, 15·5. $Ni(C_{11}H_8O_2)_2,4H_2O$ requires Ni, 12·4; $4H_2O$, 15·2%]. The dehydrated substance showed the same solubilities and the salt separated in this form from the last three solvents.

Acid nickel α-naphthoate was formed together with the normal salt by the action of nickel carbonate (0·25 g.) on the acid (2 g.) in alcohol (15 c.c.) for 6 months; the acid salt was found in the alcoholic solution, and was purified by solution in acetone, from which it separated as a dihydrate in pale green prisms, m. p. 135° (decomp.) [Found: Ni, 9·2; loss at 100°, 5·9. $Ni(C_{11}H_8O_2)_2,C_{11}H_9O_2,2H_2O$ requires Ni, 9·6; $2H_2O$, 5·9%]. It was very

soluble in alcohol, acetone, chloroform, benzene, and ether, separating from the last three as a glassy solid. When heated, it gave off α-naphthoic acid. The anhydrous substance showed the same solubilities.

Nickel β-*naphthoate* was formed when the acid (2 g.) and nickel carbonate (0·5 g.) were boiled together in water (20 c.c.) for 3 hours, pale green prisms of the trihydrate separating from the filtered solution at 0°. From boiling water this hydrate separated in flakes; it was also precipitated by the action of nickel nitrate solution on a neutral solution of the ammonium salt [Found: Ni, 13·07; loss at 150°, 12·06. $Ni(C_{11}H_8O_2)_2,3H_2O$ requires Ni, 12·9; $3H_2O$, 11·9%]. It was soluble in, but decomposed by, acetone, with the formation of an acid salt in solution and a basic precipitate; and decomposed by benzene, ether, or chloroform, to form a basic precipitate and β-naphthoic acid in solution.

Acid nickel β-*naphthoate* was formed by the action of acetone on nickel β-naphthoate crystals, the substance obtained from the acetone solution being repeatedly redissolved in small quantities of acetone until no residue formed on evaporation. The crystals of dihydrate produced were then completely soluble in acetone, ether, benzene, and chloroform and separated from the last three as a glassy solid, m. p. 148° (decomp.) [Found: Ni, 9·5; loss at 100°, 6·0. $Ni(C_{11}H_8O_2)_2,C_{11}H_9O_2,2H_2O$ requires Ni, 9·6; $2H_2O$, 5·9%]. The anhydrous substance showed the same solubilities.

Basic nickel β-*naphthoate* was formed as a pale green precipitate by the action of acetone on the normal salt. After drying at 100°, it was insoluble in water and all organic solvents [Found: Ni, 18·1. $3Ni(C_{11}H_8O_2)_2,Ni(OH)_2$ requires Ni, 18·1%].

Copper Salts of α-*Naphthoic Acid.*—(1) *Copper* α-*naphthoate monoalcoholate* (1·4 g.) was produced when α-naphthoic acid (1·3 g.) in alcohol (20 c.c.) and basic copper carbonate (1 g.) were boiled for 5 mins. and set aside for a week. It formed dark green needles containing 1 EtOH, and was recrystallised from alcohol containing the free acid [Found: Cu, 14·0; loss at 100°, 10·5. $(C_{11}H_7O_2)_2Cu,C_2H_6O$ requires Cu, 14·2; C_2H_6O, 10·2%]. These were very soluble in acetone, and from the solution dark green plates, containing 1 $COMe_2$, separated [Found: Cu, 13·8; loss at 100°, 12·6. $(C_{11}H_7O_2)_2Cu,C_3H_6O$ requires Cu, 13·8; C_3H_6O, 12·5%]; this *solvate* was insoluble in water, but soluble in ether, chloroform, benzene, carbon tetrachloride, alcohol, and acetone, decomposing in all these solvents except acetone to give the basic compound (see below). When heated until anhydrous, the crystals retained their colour and crystalline appearance.

(2) *Basic copper* α-*naphthoate* was precipitated when a solution of the normal salt in alcohol was boiled; after being washed with alcohol and acetone and dried at 100°, it formed a blue amorphous solid [Found: Cu, 25·1. $(C_{11}H_7O_2)_2Cu,Cu(OH)_2$ requires Cu, 25·4%], soluble in ammonia, from which it was deposited, on evaporation of the ammonia, as a dark blue, amorphous solid. It was insoluble in alcohol, water, and all organic solvents. On heating, it retained its blue colour until it charred.

Copper Salts of β-*Naphthoic Acid.*—(1) Copper β-naphthoate (0·9 g.) was produced as a Wedgewood-blue precipitate when a solution of the acid (0·75 g.) in alcohol (20 c.c.) was kept for 1 week in contact with basic copper carbonate (0·5 g.). After being dissolved in boiling acetone and filtered from the precipitated basic salt, it separated on cooling in prisms of the same colour, which were washed with alcohol [Found: Cu, 15·7. $(C_{11}H_7O_2)_2Cu$ requires Cu, 15·66%]. The same substance was precipitated from the acetone solution, in fine green needles, by addition of alcohol. It was slightly soluble in water, from which small, blue, anhydrous prisms were obtained on evaporation (Found: Cu, 15·8%), and was insoluble in all organic solvents, except acetone, which decomposed it into the insoluble basic compound (see below) and an acid substance which formed a deep blue solution in the acetone. On heating, the crystals kept their shape and lustre, but turned green.

(2) *Acid copper* β-*naphthoate*, of noteworthy composition, was formed when the normal salt was shaken with acetone at 35°, the solution filtered, and kept without evaporation overnight at 12°. Large peacock-blue prisms were formed, which when heated to 100° crumbled to powder but did not lose weight [Found: Cu, 13·5. $3(C_{11}H_7O_2)_2Cu,C_{11}H_8O_2$ requires Cu, 13·7%]. At higher temperatures β-naphthoic acid sublimed.

(3) *Basic copper* β-*naphthoate* was produced when a solution of the normal salt (1 g.) in acetone (150 c.c.) was refluxed until nearly colourless. The precipitate was boiled with fresh acetone, filtered off, washed with alcohol and ether, and dried at 100° [Found: Cu, 25·3. $(C_{11}H_7O_2)_2Cu,Cu(OH)_2$ requires Cu, 25·4%]. When this was dissolved in aqueous ammonia and set aside until the solution became colourless, it was regenerated as deep blue crystals (Found: Cu, 25·6%). The precipitated basic salt was a pale blue powder, insoluble in water and organic solvents; on heating, it retained its blue colour until it charred.

Nickel p-*toluenesulphinate* was formed as a pale cream precipitate when nickel carbonate (0·6 g.) was kept for a week in an alcoholic solution of the acid (3 g.); it was insoluble in alcohol, and very sparingly soluble in water, from which it separated in cream anhydrous flakes [Found: Ni, 16·0. $Ni(C_7H_7SO_2)_2$ requires Ni, 16·0%].

Nickel p-*toluenesulphonate* was formed when a current of air was passed through the above sulphinate, suspended in alcohol, until a clear, pale green solution was produced (*ca.* 6 hours). It was also prepared by the action of nickel carbonate on the sulphonic acid. It was very soluble in water, from which it separated in pale green needles of the *hexahydrate*. At 100° it lost $4H_2O$, crumbling to a white powder, and it became completely dehydrated at 180° [Found: Ni, 11·5; loss at 100°, 14·3, 14·4, 14·4; loss at 180°, 21·1. $Ni(C_7H_7SO_3)_2,6H_2O$ requires Ni, 11·5; $4H_2O$, 14·15; $6H_2O$, 21·2%].

Salts of α-*Naphthalenesulphinic Acid.*—(1) *Copper* α-*naphthalenesulphinate* was formed as a greenish-yellow precipitate by the action of copper carbonate (0·87 g.) on the acid (3 g.) in boiling alcohol or ether [Found:

Cu, 13·8. $Cu(C_{10}H_7\cdot SO_2)_2$ requires Cu, 14·2%]. It was soluble in cold water, from which it separated on boiling in bright yellow, crystalline flakes (Found: Cu, 13·8%). From the saturated solution at 0°, very pale blue prisms of a *hexahydrate* were deposited [Found: Cu, 11·2; loss at 45°, 19·4. $Cu(C_{10}H_7SO_2)_2,6H_2O$ requires Cu, 11·5; $6H_2O$, 19·5%]. This hydrate was also precipitated by addition of copper nitrate to a neutral solution of the ammonium salt of the acid.

(2) *Nickel α-naphthalenesulphinate dihydrate* was formed as a very pale cream precipitate by the action of nickel carbonate (0·69 g.) on the acid (2·4 g.) in boiling ether. The fine precipitate was separated by decantation, and freed from the sulphonate by thorough washing with water [Found: Ni, 12·3; loss at 100°, 7·6. $Ni(C_{10}H_7SO_2)_2,2H_2O$ requires Ni, 12·3; $2H_2O$, 7·55%]. It was soluble in boiling water, from which pale green plates of a *tetrahydrate* separated on evaporation [Found: Ni, 11·5; loss at 100°, 13·9. $Ni(C_{10}H_7SO_2)_2,4H_2O$ requires Ni, 11·45; $4H_2O$, 14·0%]; this was insoluble in alcohol and acetone.

Salts of β-Naphthalenesulphinic Acid.—(i) The *copper* salt was formed as a yellow precipitate by the action of copper carbonate (0·5 g.) on the acid (2 g.) in warm alcohol [Found: Cu, 14·1. $Cu(C_{10}H_7SO_2)_2$ requires Cu, 14·2%]. It was insoluble in organic solvents, very sparingly soluble in alcohol, and sparingly soluble in boiling water, from which it crystallised on cooling in bright green plates of a *dihydrate* [Found: Cu, 13·0; loss at 100°, 7·5. $Cu(C_{10}H_7SO_2)_2,2H_2O$ requires Cu, 13·2; $2H_2O$, 7·5%]. A bright yellow precipitate, rapidly turning into the green dihydrate on the filter, was obtained by addition of copper nitrate to a neutral solution of the ammonium salt of the acid. On dehydration the dihydrate retained its green colour.

(ii) The *nickel* salt was obtained as a pale green, granular precipitate by the action of nickel carbonate on excess of the acid in alcoholic solution, and was washed with alcohol and benzene [Found: Ni, 13·5. $Ni(C_{10}H_7SO_2)_2$ requires Ni, 13·3%]. It was insoluble in water, alcohol, and all organic solvents.

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50. *Decomposition Reactions of the Aromatic Diazo-compounds. Part X. Mechanism of the Sandmeyer Reaction.*

By WILLIAM A. WATERS.

Decomposition reactions of the aromatic diazo-compounds are classified into three types: (I) Decompositions of diazonium kations, giving aryl kations. (II) Decompositions of covalent diazo-compounds, giving two neutral radicals. (III) Catalysed decompositions of diazonium kations, involving a single-electron transference and yielding neutral aryl radicals: $ArN_2^+ + e \longrightarrow Ar\cdot + N_2$.

The Sandmeyer and the Gattermann reaction are considered to be of Type III, and are represented as involving cyclical electron transferences facilitated by the easy release of an electron from a cuprous kation or from metallic copper.

An examination of relative oxidation–reduction potentials affords an explanation of the *almost* unique character of cuprous salts, and of copper, and a discussion of the side reactions which occur in diazo-decompositions of this group further substantiates the view that transient neutral aryl radicals are involved.

The further possible extension of this theory of reaction catalysed by single-electron transference is indicated.

IN Parts I—IX (J., 1937, 133 to J., 1939, 1805) it was shown that many of the decomposition reactions of the aromatic diazo-compounds in non-aqueous solvents were of non-ionic type, and, in particular, that they were influenced by the presence of free metals. Extension of this work to include an experimental study of the complex salts of the diazo-compounds, especially those of copper, had been planned, with the object of elucidating the mechanism of the Sandmeyer and the Gattermann reaction, but the prosecution of this work has been delayed. In consequence of the recent publication, by Hodgson, Birtwell, and Walker (J., 1941, 771) of "An interpretation of the Sandmeyer reaction," however, it has been felt that tentative conclusions as to the mechanism of the Sandmeyer reaction, reached in consequence of the investigations mentioned above, should now be put forward, since they implement considerably the suggestions made hitherto, and may be of value in stimulating future experimental work.

Classification of Diazo-reactions.—The decomposition reactions of aromatic diazo-compounds in aqueous solution can be classified into three distinct groups:

Type I. Decompositions in acid solution, leading to the formation of phenols:

$$Ar\cdot N_2X + H_2O = Ar\cdot OH + N_2 + HX$$

This is undoubtedly a decomposition of a diazonium kation, $(ArN_2)^+$, since the rate of evolution of nitrogen

is independent of the nature of the radical X (Cain, *Ber.*, 1905, **38**, 2511; Cain and Nicoll, J., 1902, **81**, 1412; 1903, **83**, 206, 470; Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 1940, **36**, 948).

Type II. Non-ionic decompositions of aryl diazo-hydroxides, Ar·N:N·OH, which can exist in neutral and slightly alkaline solutions, *e.g.*,

$$Ar{\cdot}N_2OH + C_6H_6 \longrightarrow Ar{\cdot}C_6H_5$$
$$Ar{\cdot}N_2OH + C_5H_5N \longrightarrow Ar{\cdot}C_5H_4N$$
$$Ar{\cdot}N_2OH + Na_2HAsO_3 \longrightarrow Ar{\cdot}AsO(ONa)_2$$

(for discussion of mechanisms, see Grieve and Hey, J., 1934, 1799 *et seq.*; Haworth, Heilbron, and Hey, J., 1940, 349, 358; Waters, J., 1937, 2014; Bart, *Annalen*, 1922, **429**, 55).

Type III. Reactions such as $Ar{\cdot}N_2Hal \longrightarrow Ar{\cdot}Hal + N_2$, which can occur in acid solution and usually need a special catalyst, such as a cuprous salt (Sandmeyer reaction) or metallic copper (Gattermann reaction). Reactions of this type occur under conditions in which diazonium kations and not covalent diazo-hydroxides must be involved, yet they have many characteristics in common with reactions of Type II (see below). *It is suggested that these reactions are non-ionic decompositions of diazonium kations, brought about by a single-electron transference from a catalyst.*

Mechanism of the Sandmeyer Reaction.—Hodgson, Birtwell, and Walker (*loc. cit.*) have recently given strong support for Hantzsch's view (Hantzsch and Blagden, *Ber.*, 1900, **33**, 2544) that Sandmeyer reactions are essentially decompositions of complex cuprous-diazonium salts, $(ArN_2,Cu_2)X_3$ (for empirical formulæ, see Lellmann and Remy, *Ber.*, 1886, **19**, 810; Hantzsch, *Ber.*, 1895, **28**, 1751), in which the halide anions, X, can be exchanged with others from the surrounding solution, but they have not been able to suggest why the *cuprous* double salts decompose in a way which is so very different from the double salts which diazonium halides readily form with the halides of other metals, such as zinc, cadmium, mercury, arsenic, antimony, or bismuth: $(ArN_2)_2ZnCl_4$, $(ArN_2)_2SbCl_5$, etc. These double salts, amongst which one should include the sparingly soluble borofluorides, $Ar{\cdot}N_2BF_4$, decompose in the presence of water to give phenols, and yield appreciable percentages of aryl halides only when they are heated in the absence of water (Griess, *Annalen*, 1866, **137**, 52; Schwechten, *Ber.*, 1932, **65**, 1605), *i.e.*, in circumstances in which benzenediazonium halides can themselves give fairly high yields of aryl halides (Waters, J., 1937, 2007).

In view of the fact that cuprous salts will form addition complexes with covalent azo-compounds such as azomethane (Diels and Koll, *Annalen*, 1925, **443**, 262), it could be suggested that the cuprous diazonium halides are structurally different from all other metal diazonium halides, and that they contain a covalent azo-group, *e.g.*, (I), which might decompose to give neutral aryl radicals, but the fact that metallic copper can be used instead of a cuprous salt greatly weakens the plausibility of this *ad hoc* suggestion.

Ar—N—N—Cl
Cl—Cu—Cu—Cl
(I.)

The hypothesis that Sandmeyer reactions are oxidation and reduction processes involving the production of neutral radicals from diazonium kations does enable one to explain (*a*) the unique character of cuprous salts as catalysts, and (*b*) the course of the principal side reactions, without introducing any special structural formulæ for intermediate reaction complexes.

It is obvious that the diazonium kation, $Ar{-}\overset{+}{N}{\equiv}N{:}$, can only decompose *per se* to give nitrogen gas and an aryl kation, since both electrons of the Ar—N link must be transferred to the nitrogen atom to give the stable N_2 molecule:

$$(Ar : N : : : N :)^+ \longrightarrow Ar^+ + : N : : : N :$$

and there can be no reason for doubting that aryl kations will, like alkyl kations, *e.g.*, CH_3^+, react exceedingly rapidly with water molecules to give phenols:

$$Ar^+ + HOH \longrightarrow Ar{-}OH + H^+$$

(compare the unimolecular hydrolysis of many alkyl halides; Hughes and Ingold, J., 1933, 1571; 1935, 244, *et seq.*), even if other stable anions (*e.g.*, Cl^-) are abundantly present in the solution.

To obtain a neutral aryl radical from a diazonium kation one must supply one additional electron:

$$(Ar : N : : : N :)^+ + e \longrightarrow Ar\cdot + : N : : : N :$$

This can be provided by a *reducing agent* such as a cuprous kation,

$$Cu^{\cdot +} + Ar{-}N{\equiv}N : \longrightarrow Cu^{++} + Ar\cdot + : N{\equiv}N : \quad . \ . \ . \ . \ . \ . \quad (A)$$

and this electron transfer can easily occur within the complex kation of a cuprous-diazonium double salt. If a neutral aryl radical is formed in an (acid) aqueous solution containing halide anions in abundance,

then an aryl halide molecule can be formed by process (*B*), which entails an electron release, if there is available also an electron acceptor.

$$Ar\cdot + (:\ddot{Cl}:)^- \longrightarrow Ar:\ddot{Cl}: + e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

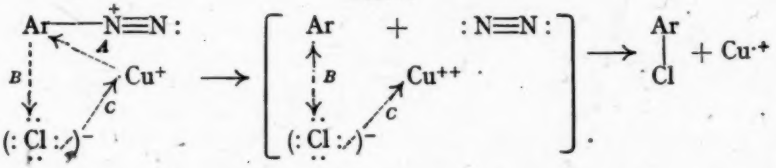
Some implications of the oxidising action of neutral aryl radicals in aqueous solution have already been discussed by the author (J., 1937, 2015) when proposing a mechanism for the Bart reaction. From the experimental evidence then advanced it would seem that a neutral aryl radical does not necessarily react immediately with the first water molecule which it encounters, and the fact that the electron affinity of chlorine (93 kg.-cals.) is less than the energy of fission of an O–H bond (110 kg.-cals.) may be adduced to support the view that reaction with halide anions (excepting fluoride) is more facile than reaction with water molecules.

In the Sandmeyer reaction the local halide anion concentration of the double salt is necessarily very high. Moreover, the electron released by process (*B*) can be accepted by the cupric kation formed in process (*A*):

$$e + Cu^{++} \longrightarrow Cu^{\cdot +} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

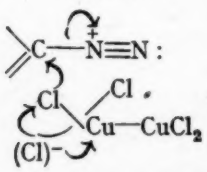
so that the whole cycle involving single-electron transference can take place within the immediate locus of the complex cuprous diazonium salt (Fig. 1). In this diagram broken arrows (– – – –→) are used to indicate movements of single electrons. This interpretation of the mechanism of the Sandmeyer reaction differs from that of Hodgson and his colleagues (*loc. cit.*), who suggested that electron transfer takes place in reverse of phase (*B*) above, and postulated that there is an electron release at the significant carbon atom of the aryl group from a chlorine atom of a complex anion (Cu_2Cl_4).

FIG. 1.



The electron transferences postulated by Hodgson and his colleagues can, in fact, be represented adequately by Fig. 2 in which the (full) curved arrows represent movements of *pairs* of electrons, and, apart from the implicit view that the covalent (= co-ordinate) copper-to-chlorine links of the complex anion $(Cu_2Cl_4)^{--}$ are concerned in this reaction process, this ionic mechanism gives no indication as to why cuprous double salts alone should decompose in this way. The author would suggest that the reaction mechanism of Hodgson *et al.* is cogent for the thermal decomposition of solid diazonium salts (see above) and that this should be classed as an ionic reaction of Type I.

FIG. 2.



The Unique Character of the Cuprous Diazonium Halides.—The single-electron transfer mechanism (Fig. 1) for the Sandmeyer reaction does explain the experimental fact that cuprous salts are almost unique in promoting reactions of Type III, since: (i) Metallic kations of constant valency, such as Na^+, Zn^{++}, Al^{+++}, cannot act as electron sources; neither can kations in their highest state of oxidation, *e.g.*, Cu^{++}, Hg^{++}, Fe^{+++}, Sn^{IV}, Au^{+++}, Pt^{IV}. (ii) The oxidation potential for the release of an electron from the kations of other transition elements is far too high for the change to occur easily in acid media:

contrast $Mn^{++} \longrightarrow Mn^{+++}$	oxidation potential	about	+ 1·5 volts
$Ni^{++} \longrightarrow Ni^{+++}$	,,	,,	very high
$Co^{++} \longrightarrow Co^{+++}$	,,	,,	+ 1·8 volts
$Fe^{++} \longrightarrow Fe^{+++}$	,,	,,	+ 0·75 volt
with $Cu^+ \longrightarrow Cu^{++}$	,,	,,	+ 0·2

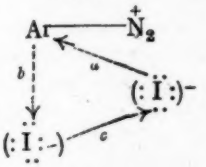
The stannous kation (oxidation potential *ca.* — 0·4 volt) is too powerful a reducing agent in acid solution, and converts diazonium kations into aryl hydrazines, whilst As^{+++}, Sb^{+++}, and Bi^{+++} are too feeble reducing agents in acid solution. In neutral solution As^{+++} and Sb^{+++} can be oxidised more easily: in these circumstances they do react with aromatic diazo-compounds, and undergo a valency change (Bart and Schmidt reactions; Type II: for mechanism compare Waters, J., 1937, 2014). (iii) Since silver, lead, mercurous, and thallous halides are insoluble in water and acids, these metals cannot be used for the preparation of aryl halides.

It is well known that the oxidation potential of a transition element can be altered by the formation of complex co-ordinated ions; *e.g.*, oxidation of bivalent nickel and cobalt kations is facilitated by their conversions into double cyanides. Hence, it is not surprising that nickel diazonium cyanides decompose to give excellent yields of aromatic nitriles (Korczynski, Mrozinski, and Vielan, *Compt. rend.*, 1920, **171**, 182; Korczynski and Fandrich, *ibid.*, 1926, **183**, 421), and cobalt salts can be used for the preparation of thiocyanates.

The oxidation potential for the initial phase (*A*) of the Sandmeyer reaction necessarily depends upon the nature of the aryl radical which accepts the extra electron, and from qualitative evidence it would appear that the presence of electrophilic substituents (NO_2, Halogens) favours the attainment of high yields. Since the oxidation potential of a solution depends upon its acidity, and upon ionic concentrations, many avenues for exact study of reaction yields immediately suggest themselves.

Analogues of the Sandmeyer Reaction.—The oxidation potential of the iodide anion is not very much higher than that of the cuprous kation, and consequently it is not surprising that the reaction $Ar{\cdot}N_2I = ArI + N_2$ can be effected without the use of a copper salt. As Hodgson and his colleagues have pointed out, the fact that this decomposition is facilitated by the presence of iodine or of copper salts supports the hypothesis that oxidation (*a*) and reduction (*b*) processes are involved (Fig. 3). Other reactions in which oxidisable anions can replace the diazo-group in the absence of copper salts are the decomposition of diazonium perbromides, and the reactions of diazo-compounds with thiols, xanthates, and dithiocarbamates (see Saunders, "The Aromatic Diazo Compounds," 1936, p. 159). All these salts have oxidation potentials close to that of the cuprous ion.

FIG. 3.



The Side Reactions.—The fact that symmetrical diaryls are often formed in good yield when cuprous salts are added gradually to aqueous solutions of diazonium salts is in full accord with the mechanism of the Sandmeyer reaction suggested above, for in these circumstances the frequency of occurrence of phase (*C*) (reduction of the cupric ion) would be small, and aryl radicals produced by phase (*A*) would have the greatest chance of having a free life sufficiently prolonged for them to disperse throughout the solution, meet, and dimerise. In these circumstances, too, azo-compounds are produced (Hantzsch and Blagden, *loc. cit.*). These can be considered to result from reactions between aryl radicals and diazonium kations, though in this case the primary product is still a radical which, to attain stability, must acquire an additional electron from some other molecule:

$$Ar{-}N{\equiv}N^{+} : + Ar^{\cdot} \longrightarrow Ar{-}\dot{N}{=}\ddot{N}{-}Ar$$

$$Ar{-}\dot{N}{=}\ddot{N}{-}Ar + e \longrightarrow Ar{-}\ddot{N}{=}\ddot{N}{-}Ar$$

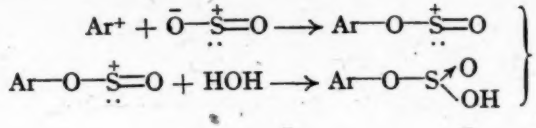
Though the production of diaryls and of azo-compounds necessitates the permanent oxidation of some of the cuprous salt, the stabilisation of the transient neutral radicals may in part be attained by more complicated chain reactions which lead to tar formation (compare Stephenson and Waters, J., 1939, 1801). The fact that both diaryls and azo-compounds are regular by-products of Sandmeyer reactions does, however, lead one to infer that these reactions are not exclusively intramolecular decompositions of complex cuprous diazonium salts, but that there are produced aryl groups which have some degree of independent existence as "free radicals." Further discussion of this topic leads, however, to questions of radical stability in solution which have been discussed recently elsewhere (Waters, *Trans. Faraday Soc.*, 1941, **37**, 770).

The Gattermann Reaction.—Gattermann's reaction (*Ber.*, 1890, **23**, 1218), in which copper powder replaces the cuprous salt, must undoubtedly be a reaction of Type III, since in all details, even in regard to the nature of the by-products, it proceeds in a similar manner to Sandmeyer's reaction. Both Gattermann (Gattermann and Cantzler, *Ber.*, 1892, **25**, 1091) and Hantzsch and Blagden (*loc. cit.*) regard the copper powder as essentially a catalyst. However, the formation of a small quantity of a copper salt is usually noticed when this reaction is carried out, and hence the cyclic scheme of Fig. 1, in which electrons easily available at the surface of metallic copper play the same part as those obtainable from cuprous ions, may justifiably be put forward, particularly since the ionisation potential for the change $Cu^{0} \longrightarrow Cu^{+} + e$ (− 0·13 volt; Nielsen and Brown, *J. Amer. Chem. Soc.*, 1928, **50**, 9) is very small indeed in acid solution, so that the reduction potentials for the initial stages (*A*) of the Sandmeyer and the Gattermann reaction would be almost identical.

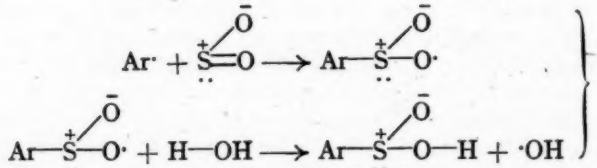
Relevant evidence in favour of the transient existence of neutral radicals in reactions of the Gattermann type are (i) that diaryls and polyaryls are frequent by-products, and occasionally major products, as in Pschorr's syntheses of phenanthrene derivatives; (ii) that the reaction can be extended to include the introduction of groups such as NO_2 and SO_2H. It then takes a way characteristic of neutral aryl groups

and not of aryls kations: from the nitrite anion one gets nitro-compounds, not aryl nitrites, and from sulphur dioxide, sulphonic acids and not sulphites, *i.e.*,

not



but



(compare the addition of sulphites to styrene; Kharasch, May, and Mayo, *J. Org. Chem.*, 1938, **3**, 175).

Though copper is by no means unique in giving up electrons to diazo-chlorides in acetone (Waters, J., 1939, 864), yet it seems as if copper were *almost* unique amongst metals for effecting the reaction $Ar—N_2^+ + M^\cdot \longrightarrow Ar^\cdot + N_2 + M^+$ in aqueous acids. From an inspection of ionisation potentials it is evident why many metals, *e.g.*, iron, nickel, or platinum, cannot replace copper, but in other cases the inertness may be due to surface-film formation (*e.g.*, halides of silver and lead). That elementary mercury can play a similar part to copper in initiating the decomposition of diazonium salts has, however, been demonstrated by McClure and Lowy (*J. Amer. Chem. Soc.*, 1931, **53**, 319). Their overall reaction, *viz.*, $Ar{\cdot}N_2Cl + Hg \longrightarrow Ar{\cdot}HgCl + N_2$, which is not quantitative, includes, naturally, chemical combination of the neutral aryl radical with the free mercury. The experimental fact that, whereas many metals will react with diazo-chlorides in acetone, ethyl acetate, or acetonitrile, yet only copper seems to be effective as a promoter of the non-ionic decomposition of the *syn*-diazocyanides (J., 1939, 1796) in a number of solvents, shows, however, that many problems concerning the critical potentials for initiating single-electron transferences remain to be solved.

Outside the sphere of the chemistry of the diazo-compounds, the facts that certain particular metals, and special salts, such as cuprous chloride and cobaltous chloride, can catalyse special reactions of Grignard reagents which are thought to involve free radicals (Gilman and Straley, *Rec. Trav. chim.*, 1936, **55**, 821; Kharasch and Field, *J. Amer. Chem. Soc.*, 1941, **63**, 2316), indicate that the theory which has been advanced above should not be regarded as a particular, *ad hoc*, hypothesis, but as a general reaction mechanism, capable of useful extension elsewhere. For instance, the discovery by Ullmann (*Ber.*, 1905, **38**, 2211; 1907, **40**, 2522; *Annalen*, 1907, **355**, 316) that a trace (1 part in 10^6 or less) of copper will catalyse the condensation between certain aryl halides and phenols or amines is explicable as a chain reaction initiated by an electron transference: $Ar—Br + Cu^{0\cdot\cdot} \longrightarrow Ar^\cdot + Br^- + Cu^{\cdot+}$. In this connection compare also Koelsch and Whitney (*J. Org. Chem.*, 1941, **6**, 795).

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51. *Some Quaternary Ammonium Salts and their Decomposition Products.*

By A. ZAKI and H. FAHIM.

p-Nitrophenyltrimethylammonium salts, previously reported to be unobtainable, and other quaternary ammonium salts containing substituted phenyl groups have now been prepared. These salts on decomposition by heat and alkali showed different behaviour according to the position and nature of the substituents.

Formation of Quaternary Ammonium Salts.—Of the three nitrodimethylanilines, the *p*-isomer previously failed to give the quaternary ammonium salt when treated with methyl iodide or methyl sulphate (Zaki, J., 1930, 1078). It has now been obtained in satisfactory yield by the use of a large excess of methyl sulphate without other solvent, or with benzene as solvent with prolonged heating.

Of the dinitrodimethylanilines, 3 : 4-dinitrodimethylaniline failed to form a quaternary ammonium salt. The 2 : 4-dinitro-compound gave in toluene solution a product from which a picrate could be precipitated. This gave satisfactory analytical figures for carbon and hydrogen, but too high a value for nitrogen.

5-Nitro-2-dimethylaminobenzenesulphonic acid, which was expected to be less resistant to addition than 2 : 4-dinitrodimethylaniline, did not react with methyl sulphate.

Attempts to get the dinitro-compounds by nitration of quaternary ammonium salts containing mononitrophenyl groups failed (cf. Vorländer and Siebert, *Ber.*, 1919, **52**, 296).

Dimethylanilines with *op*-orienting groups such as methyl and methoxyl added methyl sulphate without difficulty.

Decomposition of Phenyltrimethylammonium Salts.—The quaternary ammonium salts now investigated decomposed on heating in the same way as phenyltrialkylammonium salts (Hofmann, *Annalen*, 1851, **78**, 253; Lossen, *ibid.*, 1876, **181**, 364; Collie and Schryver, J., 1890, **57**, 767), *viz.*, $NPhR'R''R'''X \longrightarrow NPhR'R'' + R'''X$ (where X denotes a halogen and R an alkyl radical). For example, the m- and p-*nitro-*, o-*methoxy-*, o-*methyl-*, 4-*nitro*-2-*methoxy-*, and 4-*nitro*-2-*methyl-phenyltrimethylammonium chlorides* all decomposed with loss of methyl chloride and formation of the tertiary base.

On decomposition by means of sodium ethoxide as recommended by Vorländer and Spreckels (*Ber.*, 1919, **52**, 309), *m*-nitro-, *o*-methoxy-, and *o*-methyl-phenyltrimethylammonium chlorides gave the corresponding tertiary bases and methyl ethyl ether, but *p*-nitro-, 4-nitro-2-methoxy-, and 4-nitro-2-methyl-phenyltrimethylammonium chlorides gave trimethylamine and the corresponding phenetole derivatives.

o-Nitrophenyltrimethylammonium chloride, which would be expected to decompose with formation of a phenetole derivative, decomposed at once when obtained from the picrate by treatment with concentrated hydrochloric acid, giving *o*-nitrodimethylaniline hydrochloride.

Experimental.

Preparation of the Quaternary Ammonium Salts.—The salts were formed by treating the tertiary bases with methyl sulphate, neutralising the product with sodium carbonate, and finally precipitating the picrates. The chlorides were prepared by decomposing the picrates with concentrated hydrochloric acid on the water-bath, filtering and extracting the picric acid with ether, and evaporating the aqueous solutions to dryness (cf. Groenewoud and Robinson, J., 1934, 1692). The iodides were precipitated on addition of concentrated potassium iodide solution to fairly concentrated aqueous solutions of the chlorides. The perbromides were formed by adding bromine to solutions of the chlorides in glacial acetic acid or other suitable solvent; they readily lost bromine. The perchlorates were obtained by adding concentrated sodium perchlorate solution to concentrated solutions of the chlorides; they exploded above their m. p.'s.

Decomposition of the Quaternary Ammonium Salts.—The quaternary ammonium chlorides were heated above their m. p.'s. Decomposition with alkali was effected by refluxing the quaternary ammonium chloride (1 mol.) with sodium (about 1·5 atom.) dissolved in absolute alcohol. The products of decomposition in both cases were identified by the method of mixed melting points.

p-*Nitrophenyltrimethylammonium picrate*, obtained in 72% yield after *p*-nitrodimethylaniline (50 g.), methyl sulphate (50 g.), and benzene (150 c.c.) had been refluxed for 7½ hours, crystallised from water in yellow needles, m. p. 182—183° (Found: C, 43·9; H, 3·8; N, 17·3. $C_{15}H_{15}O_9N_5$ requires C, 44·0; H, 3·7; N, 17·1%).

The *chloride* crystallised from absolute alcohol–ether in white needles, m. p. 183—184° (decomp.) (Found: C, 49·8; H, 6·3; Cl, 16·3. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0; Cl, 16·4%). The *iodide* crystallised from water in yellow prisms, m. p. 161° (decomp.) (Found: I, 41·05. $C_9H_{13}O_2N_2I$ requires I, 41·2%). The perbromide formed yellow needles from absolute alcohol, m. p. 154—157° (decomp.). The *perchlorate*, crystallised from acetone–ether, had m. p. 181—182° (Found: Cl, 12·5. $C_9H_{13}O_6N_2Cl$ requires Cl, 12·65%).

o-*Nitrophenyltrimethylammonium picrate*, obtained after *o*-nitrodimethylaniline (35 g.) had been heated with methyl sulphate (140 c.c.) on the water-bath for 4 hours, formed yellow needles from water, m. p. 167—168° (decomp.) (Found: C, 44·2; H, 3·8; N, 17·4%).

m-Nitrophenyltrimethylammonium picrate, obtained in 67% yield after *m*-nitrodimethylaniline (10 g.) and methyl sulphate (10 g.) had been heated in benzene (30 c.c.) on the water-bath for 7½ hours, crystallised from water in yellow needles, m. p. 150—151° (Vorländer and Siebert, *Ber.*, 1919, **52**, 295).

The *chloride* crystallised from water in white needles, m. p. 230—235° (decomp.) (Found: C, 49·8; H, 6·1; Cl, 16·3. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0; Cl, 16·4%). The perbromide formed yellow plates, m. p. 120° (decomp.).

o-Methoxyphenyltrimethylammonium chloride, as separated in aqueous solution in the manner described above, could not be freed from adhering hydrochloric acid (cf. Groenewoud and Robinson, J., 1934, 1695).

The *perchlorate* separated from alcohol in white feathery crystals, m. p. 224—225° (Found: Cl, 13·2. $C_{10}H_{16}O_5NCl$ requires Cl, 13·4%).

4-*Nitro*-2-*methoxyphenyltrimethylammonium picrate*, obtained after 5-nitrodimethyl-*o*-anisidine (19 g.) had been heated with methyl sulphate (50 c.c.) on the water-bath for 7 hours (dilution with benzene or toluene inhibited addition altogether), crystallised from water in yellow needles, m. p. 174—175° (Found: C, 43·8; H, 4·0; N, 16·1. $C_{16}H_{17}O_{16}N_5$ requires C, 43·7; H, 3·9; N, 15·9%).

The *chloride* crystallised from alcohol–ether in white needles, m. p. about 183° (decomp.) (Found: C, 48·6; H, 6·15; Cl, 13·9. $C_{10}H_{15}O_3N_2Cl$ requires C, 48·7; H, 6·1; Cl, 14·4%), and the *iodide* in yellow needles, m. p. 156—157° (decomp.) (Found: I, 37·8. $C_{10}H_{15}O_3N_2I$ requires I, 37·6%). The *perchlorate* crystallised from acetone–ether in white prisms, m. p. 207—208° (Found: Cl, 11·3. $C_{10}H_{15}O_7N_2Cl$ requires Cl, 11·4%). The perbromide crystallised from absolute alcohol in orange needles, m. p. 135° (decomp.).

o-Tolyltrimethylammonium chloride separated with adhering hydrochloric acid. It crystallised from absolute alcohol–ether in cubic crystals which were still impure and melted at 84—85° (cf. Groenewoud and Robinson, *loc. cit.*).

The iodide crystallised from water in long, pale yellow prisms which volatilised at 225° (Found: C, 43·3; H, 5·8; I, 45·8. Calc. for $C_{10}H_{16}NI$: C, 43·3; H, 5·8; I, 45·85%) (cf. Braun, *Ber.*, 1916, **49**, 1107). The *perchlorate*, crystallised from acetone–ether, had m. p. 198—199° (Found: Cl, 14·1. $C_{10}H_{16}O_4NCl$ requires Cl, 14·2%).

4-*Nitro*-2-*methylphenyltrimethylammonium picrate*, obtained after 5-nitrodimethyl-*o*-toluidine (19 g.) had been heated with methyl sulphate (70 c.c.) and a little magnesium oxide on the water-bath for 10 hours, crystallised from acetone–ether in tiny yellow needles, m. p. 197—198° (decomp.) (Found: C, 45·5; H, 4·0; N, 16·6. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0; N, 16·5%).

The *chloride* crystallised from absolute alcohol–ether in white feathery needles, m. p. 174—175° (decomp.) (Found: C, 52·1; H, 6·8; Cl, 15·45. $C_{10}H_{15}O_2N_2Cl$ requires C, 52·1; H, 6·5; Cl, 15·4%), the *iodide* from absolute alcohol in yellow fan-like crystals, m. p. about 145° (decomp.) (Found: I, 39·0. $C_{10}H_{15}O_2N_2I$ requires I, 39·4%), the *perchlorate* from water in white needles, m. p. 186—187° (Found: Cl, 12·3. $C_{10}H_{15}O_6N_2Cl$ requires Cl, 12·05%), and the perbromide from glacial acetic acid in orange crystals, m. p. 121—122° (decomp.).

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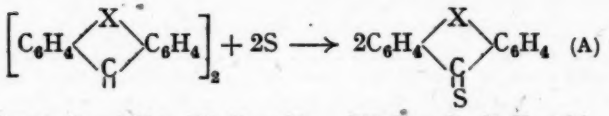
52. *Cleavage of the Ethylene Linkage by the Action of Sulphur.*

By ALEXANDER SCHÖNBERG and (MISS) WAFFIA ASKER.

Dithioxanthylen (III), diflavylen (VI), and dithioflavylen (VII) react with sulphur at about 280° with the formation of the corresponding thioketones; for example, dithioflavone (XII) is formed from (VII), and thioxanthione (V) from (III) (compare scheme A). A theory based on resonance is proposed to explain these reactions. Dixanthylen (I), dithioxanthylen (III), dithioflavylen (VII), $\alpha\alpha'\alpha''\alpha'''$-tetraphenyl-$\gamma\gamma'$-dithiopyrylen (VIII) and its chloro-derivative (IX) were obtained by treating the corresponding ketones (example, xanthone in the case of dixanthylen) with thionyl chloride, followed by the action of copper bronze. In the case of dithioflavylen (VII) an intermediate compound was obtained for which formula (XVI) or (XVII) is proposed.

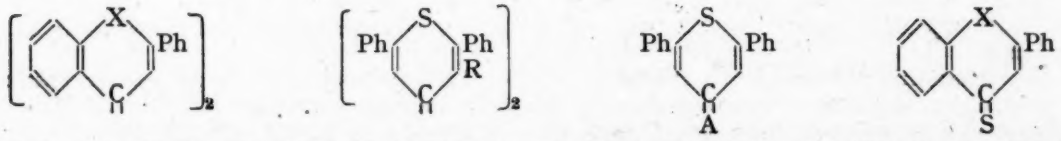
FISSION of the ethylene linkage in dixanthylen (I) by the action of sulphur with the formation of xanthione (IV) (Schönberg, *Ber.*, 1925, **58**, 1796) takes place quickly at 280°. Gleu and Schaarschmidt (*Ber.*, 1939, **72**, 1246) reported on a similar reaction of (II). The present paper deals with the substances (III), (VI),



(A)

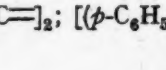
(I, X = O; II, X = NMe; III, X = S.) (IV, X = O; V, X = S.)

(VII), and (VIII), of which (III), (VI), and (VII) reacted with sulphur at about 280° according to scheme (A).

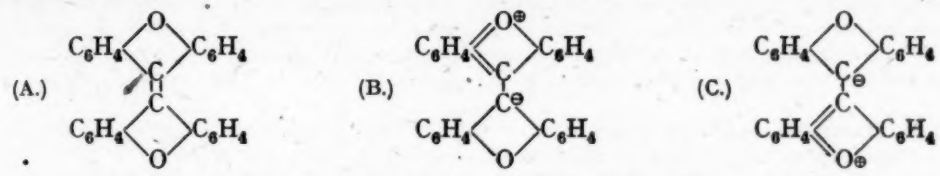


(VI, X = O; VII, X = S.) (VIII, R = H; IX, R = Cl.) (X, A = S; XI, A = O.) (XII, X = S; XIII, X = O.)

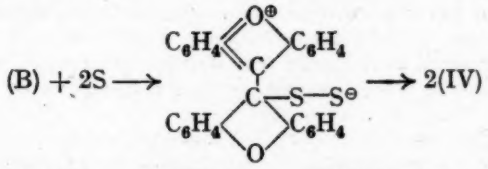
Explanation of the Sulphur Cleavage Reaction.—As the substances listed below do not form thioketones when acted upon by sulphur [Schönberg: "Thioketone, Thioacetale und Aethylensulphide," Sammlung chemischer und chemisch technischer Vorträge, Verlag Ferdinand Enke, p. 29 (1933)], it is reasonable to attribute the sensitivity of the central ethylene linkage in the substances (I), (II), (III), (VI), and (VII) to their hetero-ring atoms.

$Ph_2C{:}CPh_2$; $[(p\text{-}MeO\cdot C_6H_4)_2C{=}]_2$; $[(p\text{-}C_6H_5\cdot C_6H_4)_2C{=}]_2$;  $[(p\text{-}NMe_2\cdot C_6H_4)_2C{=}]_2$.

The actual ground state of the dixanthylen molecule above 280° is possibly a resonance hybrid involving the forms A, B, and C :



and the cleavage of dixanthylen by sulphur can be illustrated according to the scheme :



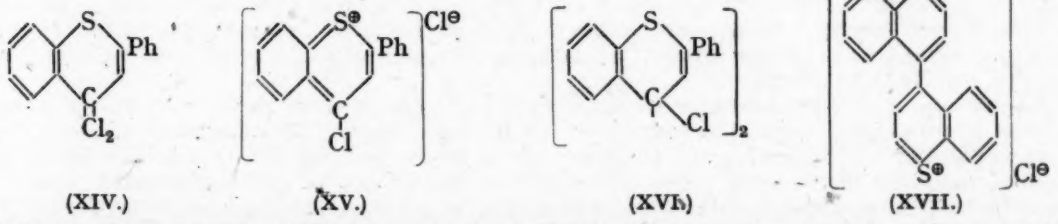
For another possible explanation, see Schönberg and Nickel (*Ber.*, 1931, **64**, 2323). Our failure to perform the sulphur cleavage reaction on (VIII) is explained by the fact that (X), which should be the product, loses sulphur easily at 145° with the formation of (VIII) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1646).

Dithioxanthylen (III) and dithioflavylen (VII) were changed only very slightly or not at all when air was passed through their solutions in benzene (thiophen-free) for 10 hours at room temperature.

The yellow crystals of diflavylen (VI), but not those of dithioflavylen (VII), when pressed in a mortar, gave a dark red colour which changed to yellow again on the addition of a drop of ether. We cannot suggest an explanation for this phenomenon.

Preparation of Dichromylen, Dipyrylen, Dixanthylen, their Derivatives, and their Sulphur Analogues.—The compounds (I), (III), (VII), and (IX) were prepared by the action of copper bronze on the keto-chlorides formed when the corresponding ketones were treated with thionyl chloride (Schönberg and Nickel, *Ber.*, 1934, **67**, 1795).

It may be more correct to formulate the products obtained by the action of thionyl chloride on these ketones as salts; *e.g.*, formula (XV) instead of (XIV) should be given to the product of the action of thionyl chloride on 1-thioflavone. By the action of copper bronze on a dilute benzene solution of (XIV)



(XIV.) (XV.) (XVI.) (XVII.)

or (XV) a compound (XVI or XVII) was obtained which must be regarded as an intermediate product in the preparation of dithioflavylen (VII), since it yields (VII) on further treatment with copper bronze.

The yield obtained by the thionyl chloride method is often better than that from earlier methods. For example, dixanthylen (I), previously obtainable only in poor yield by the reduction of xanthone (Gurgenjanz and Kostanecki, *Ber.*, 1895, **28**, 2310, stated no yield), is produced in about 75% yield from xanthone.

Experimental.

Dithioflavylen (2 : 2′-*Diphenyldithiochromylen*) (VII).—1-Thioflavone (Arndt, *Ber.*, 1925, **58**, 1620) (1 g.) was treated with thionyl chloride (15 c.c.) on a water-bath for 10 hours, the excess of thionyl chloride distilled by means of the pump, and the residual dark red oil dissolved in dry benzene (50 c.c.) and refluxed for 6 hours with copper bronze (8 g.) with occasional shaking or stirring. The benzene solution was filtered hot and concentrated. Addition of light petroleum (b. p. 60—70°) precipitated dithioflavylen in yellow crystals, m. p. 285°, difficultly soluble in boiling benzene and carbon tetrachloride (giving an orange colour), and very sparingly soluble in boiling absolute alcohol. With concentrated sulphuric acid it gave a yellow solution (Found : S, 14·3. Calc. for $C_{30}H_{20}S_2$: S, 14·4%).

Dithioflavylen in glacial acetic acid was recovered unchanged after 6 hours' refluxing with water and concentrated hydrochloric acid (equal vols.).

Formation of (XVI) *or* (XVII).—The dark red oil obtained by the procedure described above (1-thioflavone, 0·5 g.; thionyl chloride, 15 c.c.) was dissolved in dry benzene (60 c.c.) and refluxed with copper bronze (4 g.) for about 6 hours, the time depending on the size of the copper bronze particles. The reddish-brown benzene solution was filtered hot and evaporated to dryness. The pink residue was crystallised from light petroleum (b. p. 100—110°), giving pale brown, feather-shaped needles, m. p. 120°, soluble in hot benzene and acetone. The substance was not obtained in a pure state (Found: S, 11·2; Cl, 12·1. Calc. for $C_{30}H_{20}Cl_2S_2$: S, 12·4; Cl, 13·5%).

A solution of this substance (0·2 g.) in dry benzene (10 c.c.) was refluxed for 3 hours with copper bronze (2 g.). On concentration of the hot filtered solution dithioflavylen (VII) was obtained.

Action of Sulphur on Dithioflavylen (VII).—Dithioflavylen (0·5 g.) was ground with sulphur (0·5 g.) and heated. The colour changed from bright yellow to deep red as soon as melting occurred. The melt was kept at 270—280° (bath temp.), allowed to cool, powdered, and extracted repeatedly with petroleum (b. p. 100—110°). The extract was concentrated, cooled, filtered from precipitated sulphur, further concentrated, and cooled. Dithioflavone (XII) crystallised in reddish-brown needles, m. p. 110°, not depressed by an authentic specimen (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1644). It gave green solutions in ether and benzene and a brown solution in alcohol.

αα′α″α‴-Tetraphenyl-γγ′-dithiopyrylen (VIII).—αα′-Diphenyl-γ-thiopyrone (XI) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1640) (0·5 g.) was treated with thionyl chloride for 10 hours as described previously. The orange-coloured oil left after distillation of the excess of thionyl chloride was dissolved in dry benzene (30 c.c.) and refluxed with copper bronze (6 g.) for 7 hours. The deep red benzene solution was filtered hot and concentrated; on addition of light petroleum (b. p. 70—80°) dark green crystals separated, m. p. about 300° (decomp.) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1640) (Found: C, 82·0; H, 4·1; S, 12·3. $C_{34}H_{24}S_2$ requires C, 82·2; H, 4·9; S, 12·9%).

The substance (VIII) was recovered unchanged after 6 hours' refluxing in absolute alcohol with N-sodium hydroxide.

ββ′-Dichloro-αα′α″α‴-tetraphenyl-γγ′-dithiopyrylen (IX).—This was prepared from β-chlorodiphenyl-γ-thiopyrone (Arndt, Nachtwey, and Pusch *Ber.*, 1925, **58**, 1640) by the method used for the preparation of (VIII). It separated from the concentrated benzene solution, on addition of light petroleum (b. p. 60—70°), in reddish-brown crystals, m. p. 282—284°, soluble in hot benzene and difficultly soluble in alcohol. With concentrated sulphuric acid, it gave a reddish-brown solution (Found: Cl, 13·1; S, 11·8. Calc. for $C_{34}H_{22}Cl_2S_2$: Cl, 12·6; S, 11·3%).

Dixanthylen (I).—Xanthone (15 g.) was dissolved in thionyl chloride at room temperature and refluxed for 8 hours. The oil obtained after distillation of thionyl chloride was dissolved in dry xylene (150 c.c.) and refluxed with copper bronze (8 g.) for 10 hours. The deep red xylene solution was filtered hot, concentrated, and cooled; dixanthylen separated in greenish-yellow needles (9·4 g.), m. p. 307°. A further 1 g. was extracted from the copper bronze with carbon disulphide.

Action of Sulphur on Dixanthylen (I).—Equal weights of dixanthylen and sulphur were ground together and heated in a wax-bath at 300° for 1 minute. After ½ minute a dark green liquid was formed. The product gave a bluish-green solution in carbon disulphide, in which mercuric chloride crystals acquired a superficial brownish-red colour after ½ hour [formation of the molecular compound of xanthione (IV) and mercuric chloride (Schönberg, *Ber.*, 1925, **58**, 1793)].

Dithioxanthylen (III).—Thioxanthone (Davis and Smiles, J., 1910, **97**, 1296) (5 g.) was treated with thionyl chloride as described previously. The deep scarlet-red oil obtained after distillation of the excess of thionyl chloride was dissolved in dry boiling xylene, copper bronze (8 g.) added, 1 g. at a time at intervals of ½ hour, and boiling continued for 10 hours. The xylene solution was filtered hot and concentrated; on cooling, dithioxanthylen (III) separated in almost white needles (3 g.), m. p. above 350° (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1384). A further 0·4 g. was obtained by extracting the copper bronze several times with boiling xylene (Found: S, 15·9. Calc. for $C_{26}H_{16}S_2$: S, 16·3%).

Dithioxanthylen was dissolved in benzene and treated with animal charcoal; colourless needles showing a blue fluorescence in the solid state and in cold benzene solution were obtained. They dissolved in boiling ethyl phthalate; the cold solution showed a blue fluorescence, which diminished rapidly on heating.

Action of Sulphur on Dithioxanthylen (III).—Dithioxanthylen (1 g.) was ground with sulphur (0·5 g.) and heated at 260—270° (bath temp.) for ½ hour. The green melt was allowed to cool, powdered, and extracted repeatedly with boiling benzene. The benzene solution was concentrated, cooled, filtered from sulphur, further concentrated, and cooled; brownish-green crystals were obtained, m. p. 168° after recrystallisation from light petroleum (b. p. 100—110°), not depressed by thioxanthione (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1382).

Action of Sulphur on Diflavylen (VI).—Diflavylen (Schönberg and Nickel, *Ber.*, 1931, **64**, 2325) (0·2 g.) was ground with sulphur (0·5 g.) and heated at 290° for 1 hour. A cold acetone extract of the product was evaporated, and the residual oil crystallised from ether–light petroleum (b. p. 30—50°). After recrystallation from light petroleum (b. p. 70—80°) it formed red needles, m. p. 86°, not depressed by authentic 4-thioflavone (XIII) (Schönberg and Nickel, *Ber.*, 1931, **64**, 2325).

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53. *Studies in the Diazotisation and Nitrosation of Amines. Part V. The Effect of lowering the Dielectric Constant of the Reaction Mixture.*

By J. Campbell Earl and Noël G. Hills.

An investigation has been made of the reaction between nitrous acid and some aliphatic amines in aqueous solutions of which the dielectric values were lowered by the presence of dioxan. The reaction, under certain conditions, appeared to be bimolecular, like that between nitrous acid and the aromatic amines in water or methanol. The behaviour of the reaction mixtures with regard to electrical conductance resembled that, described in earlier papers of this series, of reaction mixtures containing nitrous acid and aromatic amines.

The reaction between nitrous acid and amines, both aliphatic and aromatic, probably takes place in two principal stages: first, formation of an unstable complex by addition of the amine to nitrous acid, and then elimination of water from the complex with formation of an *N*-nitrosoamine, or some other product, which may or may not undergo further change. As a rule, the first of these stages is apparently much the slower of the two and therefore determines the order of the reaction. It is with this stage that the present investigation is concerned.

Fig. 1.

Dimethylamine and nitrous acid (1 : 1) *with* 0·5 *mol. of* HCl *in dioxan–water solutions.*

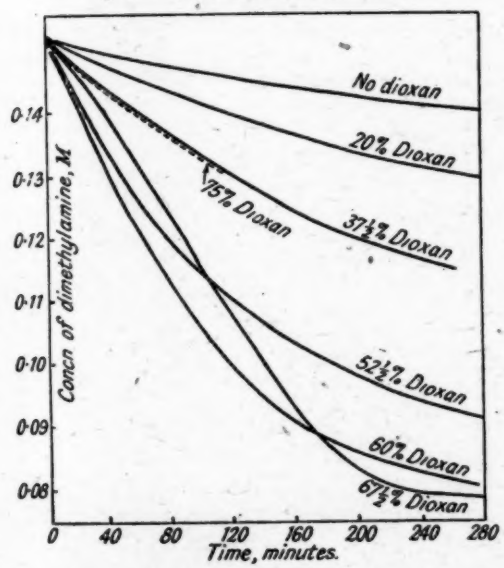
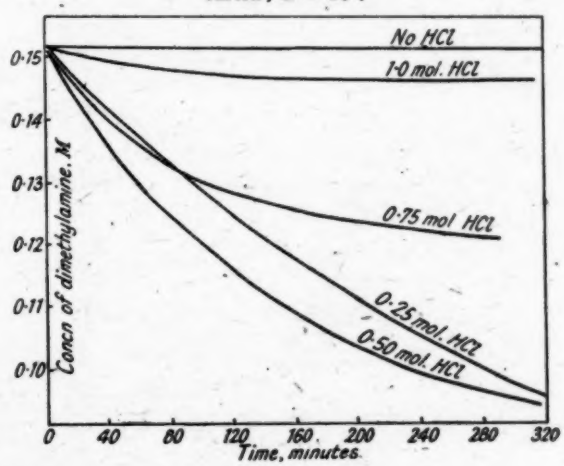


Fig. 2.

Dimethylamine and nitrous acid in 47½% *dioxan:* HCl *varied;* T = 50°.



The condition of an amine nitrite in solution is represented by the scheme

$$\mathrm{NHRR' + \overset{+}{H} + \bar{N}O_2 \rightleftharpoons \overset{+}{N}H_2RR'\,\bar{N}O_2 \rightleftharpoons \overset{+}{N}H_2RR' + \bar{N}O_2}$$
$$\Updownarrow$$
$$\mathrm{NO{\cdot}OH}$$

If the electrolytic dissociation of an amine nitrite can be suppressed, its hydrolysis into free amine and free nitrous acid will be favoured. As Kraus and Fuoss (*J. Amer. Chem. Soc.*, 1933, **55**, 21) had shown that tetra*iso*amylammonium nitrate is only feebly ionised in dioxan solution, it was decided to use water–dioxan mixtures in order to determine whether an aliphatic amine nitrite in such solvents would behave similarly to an aromatic amine nitrite in water, owing to its decreased electrolytic dissociation.

The aliphatic amines selected were dimethylamine and dibenzylamine, the latter being strictly aliphatic in respect to its imino-group. These were used with an equimolecular proportion of nitrous acid, and, as a rule, with less than this proportion of hydrochloric acid. The proportion of dioxan in the solvent was varied in different experiments, but never exceeded 75%, since this was the maximum consistent with the various solubilities at the lowest temperature used. In the experiments illustrated in Fig. 1 the concentration of the hydrochloric acid was half that of each of the other two reactants, this proportion having

been found to produce the maximum rate of reaction in water (Earl and Hills, J., 1939, 1089 *). The results show that the velocity of the reaction increases with increasing dioxan content in the solvent up to about 53%; beyond this, the accelerating effect is less in evidence in the earlier part of the reaction, but develops later, the reaction appearing to be self-catalysed.

The experiments illustrated in Fig. 2 show that, in 47·5% dioxan solution, as in aqueous solution, reaction is fastest with 0·5 mol. of hydrochloric acid, being negligible with no acid and very slow with 1·0 mol.

When the reaction with dimethylamine is followed conductimetrically in dioxan–water solutions, the same effects are observed as for methylaniline in aqueous solution (Earl and Hills, *loc. cit.*), *viz.*, an initial fall in conductivity ascribable to the disappearance of ammonium and nitrite ions, and then a more or less sudden increase in conductivity, due no doubt partly to the production of hydrogen ion from the amine hydrochloride, attacked at this stage by nitrous acid, and partly to formation of nitric acid by atmospheric oxidation of nitrous acid. That it is not solely this oxidation that is responsible for the increase in conductivity, however, is apparent from the results of experiments with pairs of identical reaction mixtures,

FIG. 3.

Dibenzylamine nitrite (0·1M) *with* 0·03M-HCl *in* 60% *dioxan*, $T = 10°$.

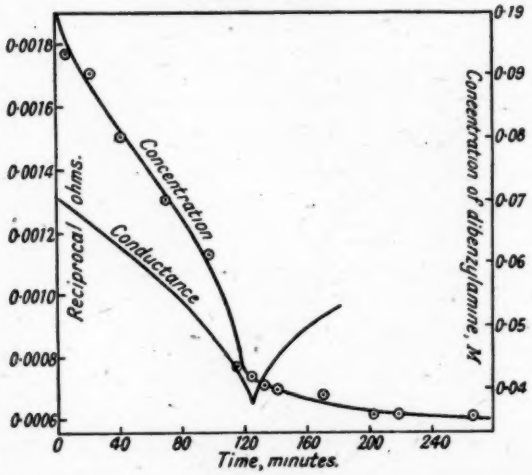
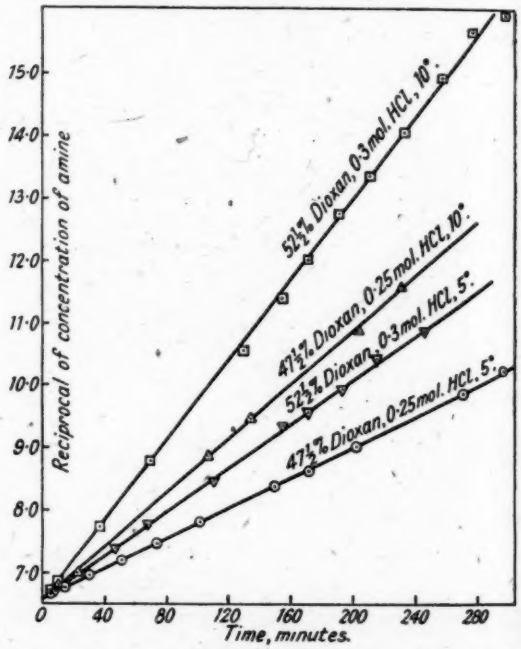


FIG. 4.

Dimethylamine and nitrous acid (*each* 0·152M) *in dioxan–water solution.*



such that in one member of each pair the reaction was followed by determining the amount of amine left at different stages, and in the other by determining the electrical conductivity from time to time. After the point at which the conductivity began to increase, the amine still continued to disappear, although more slowly than before. This effect is more pronounced with the weaker base, dibenzylamine (see Fig. 3).

The effects of different concentrations of hydrochloric acid upon the course of the reaction with dibenzylamine were also followed by conductivity measurements. The curves thus obtained were all similar to that shown in Fig. 3 and resemble more closely the methylaniline conductivity curves (Earl and Hills, *loc. cit.*) than do those for dimethylamine, but, like the dimethylamine curves for the reaction in the presence of much dioxan (cf. Fig. 1), they indicate an initial retardation.

Experiments were made to determine the order of the reaction with dimethylamine in a solvent containing rather less dioxan than would produce the maximum velocity at the temperature of the experiment. The results are shown in Fig. 4, in which the reciprocal of the amine concentration is plotted against time. There was no evidence of any irregularity such as self-catalysis. At both 5° and 10° with 47½% and with 52½% of dioxan there was evidence of a second-order reaction, as proved by the straight-line graph, provided that there was present 0·25—0·30 mol. of hydrochloric acid per mol. of amine, or nitrous acid,

* In Fig. 2 in this paper, the molecular proportions of hydrochloric acid to amine nitrite used to obtain the curves are not shown. For the curves from left to right they are 0·80, 0·20, 0·15, 0·10. The initial concentration of the nitrite should be M/100, not M/1000 as stated.

at the beginning of the experiment. More dilute solutions (*ca.* 0·075M-amine and nitrous acid) also indicated reactions of this order, but variation of the proportion of hydrochloric acid had an entirely different effect. With a higher proportion, the reaction appeared to be termolecular at first and somewhat indeterminate later; but when the proportion was diminished to 0·15 mol. per mol. of amine or nitrous acid, the reaction seemed to become unimolecular, as shown by a straight-line relationship between time and the logarithm of the amine concentration. Velocity constants are not given, since the initial concentrations of the amine and nitrous acid in the forms in which they react are conjectural, being dependent upon the equilibria existing in the reaction mixtures.

The results described therefore justify the views put forward for the mechanism, although certain features, *viz.*, the acceleration of the reaction during its earlier stage, and the change in the order of the reaction with dimethylamine brought about by altering the proportion of hydrochloric acid, require further work before they can be explained.

Experimental.

In experiments in which the rate of disappearance of dimethylamine was measured, the calculated amounts of the base and of hydrochloric acid, both in aqueous solution, were added to such a volume of the requisite dioxan–water mixture that, when the reaction was started by adding an aqueous solution of sodium nitrite equivalent to the base, the reaction mixture should be 0·150M with respect to the base and the nitrite. For conductivity measurements the reagents were made of 0·200M concentration. There was, however, a small contraction due to the mixing of the dioxan and water, the maximum effect being in mixtures containing 52½% of dioxan, so that the initial concentrations of amine and nitrite in the two sets of experiments were 0·152M and 0·203M, respectively. On account of the sparing solubility of dibenzylamine, mixtures in which it was used were made up to be 0·10M with respect to amine and nitrite.

In order to follow the change in concentration of both amines, samples were taken with a pipette (with suitable precautions on account of the toxicity of dioxan) and run into excess of sodium hydroxide solution. The amine was then distilled into standard acid and titrated in the usual manner, the methyl-red–methylene-blue achromatic indicator being used. The presence of dioxan appeared not to affect the titration in any way. Dibenzylamine proved more difficult than dimethylamine to determine exactly by this method.

The conductance of the reaction mixtures was measured in a cell of the ordinary Arrhenius type, in a Wheatstone bridge circuit suitably matched with transformers to a valve-oscillator similar to that described by Grinnell Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1049), used as the source of alternating current.

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54. *Equilibria and Changes in Metal Hydroxide Sols.*

By Henry Bassett and Reginald G. Durrant.

Hydroxide sols of aluminium, chromium, iron (III), lanthanum, neodymium, and thorium have been studied from the point of view of the nature of the stabilising ion and of the changes which they undergo on ageing.

The sols of lanthanum and neodymium hydroxides are difficult to prepare in a pure condition and to investigate owing to their sensitiveness towards carbon dioxide.

Chemical methods for determining the free and bound kations in the positive sols have been developed and their trustworthiness discussed. The micellar charges appear, as a rule, to be due to adsorbed metal ions though, in some cases, both the free and the bound kations are probably present largely as basic ions. Hydrions play a part in the equilibria in hydroxide sols, and reasons are given for considering that in some of the less basic hydroxides part of the micellar charge may be due to bound hydrions.

The micelles may in exceptional cases have a crystalline character, but as a rule they appear to be liquid or glassy so that the sols are to be regarded as emulsions. The micelles then constitute a second liquid phase with a very high metal-hydroxide concentration, and into this medium penetrate many of the peptising metal ions which are first adsorbed on the surface of the liquid or glassy micelles. The invading kations are accompanied by balancing anions which thus become masked towards reactions external to the micelle, and in many cases the kations become co-ordinated to metal hydroxide and converted into highly basic ions. If a sufficient amount and concentration of the peptising kation is available, this process may continue until the original (liquid or glassy) hydroxide has become converted into what is essentially a liquid or glassy basic salt. The latter may persist in this condition as a sol for a long time, or it may pass into true solution as a soluble basic salt or separate out as crystalline basic salt, with disappearance of the sol condition.

The chief factors determining whether a crystalline basic salt is formed in any given case would seem to be the tendency for the metal hydroxide to co-ordinate with metal ions, and the solubility and crystallising capacity of the potential basic salt.

Ageing of metal hydroxide sols is attributed mainly to one of four causes: (i) coalescence of the liquid micelles to form larger droplets, (ii) dehydration of the hydroxide constituent of the liquid micelles, (iii) crystallisation of the hydroxide either before or after dehydration, and (iv) crystallisation of the basic liquid or glassy micelle as a definite basic salt, or its passage into true solution. Which of these factors is of most importance with any particular hydroxide will depend fundamentally upon the general characteristics of the metal. Ageing is normally slow, but in ferric hydroxide sols factor (ii) causes a marked ageing.

The operation of factors (iii) and (iv) is greatly facilitated by the atomic transference rendered possible by the equilibria between free and bound kations. Crystallisation is for this reason more likely to occur in sols where the micelles have a low value for the ratio, micellar hydroxide/bound kation. The basic chlorides do not crystallise readily, but a crystalline one did separate from a thorium hydroxide sol; further, it has been possible to identify some of the basic kations occurring in aluminium hydroxide sols by making use of the sparing solubility and good crystallising power of their sulphates.

In aqueous sols with liquid micelles the bound kations are of two types, (*a*) those in solution in the micelle—these are mostly basic and are accompanied by an equivalent number of anions—and (*b*) kations adsorbed on the surface of the micelles with equivalent anions in the electrical double layer. It is to these adsorbed kations, which appear to be mainly simple hydrated ions, that the ordinary charge of the micelles is due.

THE hydroxide sols investigated (see Summary) were all positive sols, with chlorion as negative or contra-ion. Our knowledge of such sols is incomplete in several particulars, for instance, (i) the nature of the stabilising ions, (ii) the mechanism by which they are attached to the micelles, (iii) the cause of the ageing of such sols. The experiments now described, the result of 10 years' work, throw some light on these matters. It is often supposed that the charge on the micelles of positive sols is due to adsorbed hydrions, but the alternative view that it originates from adsorbed kations of the metal of the hydroxide is held by many workers. On the latter view, the peptisation of a metal hydroxide by the corresponding chloride is due, in the main, to adsorption of metal ions, and there should be an equilibrium in the sol between the free and the bound metal ions. It is, however, quite likely that, in cases where the salt is appreciably hydrolysed, adsorption of hydrion would also play some part in the process.

Study of any equilibria concerned requires therefore some method of determining the proportion of free and bound metal ion and hydrion. The electrochemical method of measuring the concentration of free ions in a sol has been widely used by Pauli and others (Pauli and Valkó, "Elektrochemie der Kolloide," 1929, p. 544) for the determination of chlorion and hydrion. It is generally considered to be the best method, as it can be applied directly to the sol itself, but, owing to the absence of suitable electrodes, it is only of restricted applicability. Analysis of the clear liquid obtained by coagulating the sols with suitably chosen electrolytes gives another method of attacking the problem which has also been used extensively by Pauli (*op. cit.*, pp. 519—531). It is this chemical method which we have chiefly used. The adsorptive capacity of the micelles present in a sol might differ from that of the coagulum obtained by the addition of electrolytes, so analysis of the liquid in contact with the curd does not necessarily give the composition of the intermicellar fluid, as has been pointed out by McClatchie (*J. Physical Chem.*, 1932, **36**, 2087). It is difficult to foresee exactly how the two would differ, though it might be thought that curding would cause a diminution of surface and consequently reduced adsorption. The concentration of the free stabilising ion found by the analytical method would then be higher than that found by the electrical method. It is also possible that the electrolyte used for coagulation might disturb the adsorption equilibria by itself entering into some exchange reaction.

Our own results appear to show that little, if any, disturbance arises from these two causes if the coagulating electrolyte is properly chosen. We believe that the analytical method then gives results very close to the truth. It was possible to test this view for the case of hydrion with one of the thorium sols (see p. 300). Sodium metaphosphate curds thorium sols, precipitating any free thorium ions present. It does not liberate any acid when added to a solution of thorium chloride. Any acid found in the filtrate from the curd thrown down by sodium metaphosphate from a thorium hydroxide sol should therefore represent hydrion originally present in the sol. Very close agreement was obtained between the value obtained in this way and by the glass electrode on the sol itself.

No similar comparison is possible in the case of the metal ions, but it seems likely that the free ions found in the filtrate, after curding by an electrolyte which precipitates only the colloidal micelle, gives a correct value for the ionic concentration of the intermicellar fluid, apart from an uncertainty as to the precise nature of these ions (see below, also pp. 281, 282). This opinion is based on the fact that certain

of the sols on coagulation gave liquids in which no measurable amount of metal ion or hydrion could be detected. This showed that no metal ion was set free on coagulation in spite of the fact that much bound kation was present, and, as indicated previously, it is more likely that the coagulum would have a smaller adsorptive capacity than the micelles rather than *vice versa*. Ammonium sulphate was found the most suitable coagulant for determination of the free metal ions present in the sols. It precipitates the micelles of all the sols (except those of chromium) when added in small excess, and has no effect on the free metal ions. Considerable excess of this coagulant can generally be added without causing complications, though in some cases it must be used with discretion (see p. 286).

We at first thought that sodium metaphosphate was a suitable electrolyte for use when determining the hydrion concentration of the sols, since it is a good coagulant for the micelles and can also precipitate the free metal ions of most of the sols; but we found that some sols, more especially those of aluminium and ferric hydroxides, appeared to have a very high acidity when examined by this method, though direct glass-electrode measurements on them showed that very little hydrion was present.

The action of sodium metaphosphate (freshly prepared by heating ammonium sodium hydrogen phosphate) on fresh solutions of aluminium or ferric chloride or sulphate was therefore examined. An amorphous basic salt was precipitated owing to hydrolytic disturbance, so the filtrate was strongly acid, the same amount of acid being indicated by the glass electrode as by titration. Excess of metaphosphate will dissolve the precipitate or prevent its formation, and also protects the aluminium or ferric salt to some extent from the action of sodium hydroxide, but not completely.

It is because of this action on the free kations that acid is found in the filtrates from the metaphosphate curds of aluminium or ferric hydroxide sols. No precipitate is thrown down during the titration with alkali even although dissolved aluminium or iron is still present. This seems to be due to peptisation of the hydroxide by metaphosphate to form a negative sol, for, when a 0·1N-aluminium sulphate solution is stirred into an equivalent amount of sodium metaphosphate solution, no precipitate is obtained, although a thick curd is formed when the mixing is done in the reverse order. A complex alumina–metaphosphate anion is probably formed when larger amounts of metaphosphate are used.

Chromium salts appeared to behave in a similar manner with metaphosphate, but there was no liberation of acid from thorium chloride.

Sodium metaphosphate can be satisfactorily used as a coagulant in determinations of the acidity of thorium sols and may give useful results for aluminium and ferric sols which contain only small amounts of free metal ions. In the last two cases, however, the values found are almost certain to be too high. Care should be taken to add only sufficient metaphosphate just to cause complete coagulation: an amount slightly less than that equivalent to the chlorion content of the sol will be required.

There is abundant evidence that some of the metals examined by us, and aluminium and chromium in particular, can form basic kations. It is probable, therefore, that, when a polyvalent kation such as $Al^{\cdot\cdot\cdot}$ (presumably as $[Al(H_2O)_6]^{\cdot\cdot\cdot}$) is adsorbed by its hydroxide, some interaction might occur to produce basic kations. It is rather exceptional, however, for positive evidence of this to be obtained by direct analysis of the sols. The importance of these basic kations is illustrated by the results obtained with aluminium hydroxide sols No. 15 and 16. If, in the case of sol No. 15 all the free aluminium found in the filtrate from the curd obtained with ammonium sulphate is calculated as $Al^{\cdot\cdot\cdot}$ it would account for all, or even a little more than, the total Cl' ions. There would then be no kations left to stabilise the micelles. This is definite evidence that some, if not all, of the free aluminium is in the form of basic kations.

Sol No. 16 illustrates the same point still more clearly, and in that case the basic kations were actually isolated as a stable crystalline sulphate. The existence of basic kations in the micelles of aluminium hydroxide sol has been considered by Pauli (*Kolloid-Z.*, 1921, **28**, 49) and by Adolf, Pauli, and Jandraschitsch (*ibid.*, 1921, **29**, 281).

Isolation of the basic kations as crystalline sulphates enables differentiation between basic and other kations to be made to some extent in the case of aluminium, but we are not aware of any general method by which this can be done for other metals. We are, for this reason, not quite sure what we have estimated by our methods as "free kation." In the tables and discussions we refer to it as free $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$, etc.; although it may not be only this and may in certain cases consist largely of basic ions.

Reasons are given later for considering that in many cases the free kations are actually present almost entirely as the simple (hydrated) ions and not as basic ions. The presence of basic kations would invalidate any electrode-potential method of measuring the kation concentration of the intermicellar fluid of hydroxide sols.

The mechanism by which free basic kations are produced must be considered. We have obtained much information on this matter from experiments with aluminium hydroxide sols and believe that the following explanation of the nature and reactions of metal hydroxide sols is consistent and satisfactory.

The majority of these sols appear to be emulsions. The second liquid phase which forms the micelles has a very high metal-hydroxide concentration and may be so viscous as to constitute a "glass." A crystalline core may be present in some cases. The peptising kations are adsorbed on the surface of the hydroxide "droplets," and the micellar charge is due almost entirely to kations which are so adsorbed and are balanced by an equivalent amount of anion in the electrical double layer. These adsorbed kations are probably hydrated and will be in equilibrium with similar ions which are free in the intermicellar fluid. Some of the adsorbed kations will, however, pass into solution in the liquid (or glass) of which the micelle is composed. The kations which do this will of necessity be accompanied by an equivalent number of anions. Although the latter remain in the ionic condition, they have been withdrawn from the intermicellar solution and have become inert towards tests carried out on this. This appears to be a reasonable cause of the masking of much of the chlorion in old ferric hydroxide sols when the chlorion was determined by the calomel electrode (Pauli and Valkó, *op. cit.*, p. 520).

If the kations which thus invade the micelles are those of the metal forming the hydroxide, there will be some tendency, varying from metal to metal, for co-ordinated water to be replaced by co-ordinated metal hydroxide. Very basic cations then result. General similarity of composition between these and the fluid constituting the micelles will lead to the basic ions or salt being much more soluble in the micellar than in the intermicellar fluid, so that, with most sols, few of these basic ions will escape from the micelles and become free. It seems likely for this reason that the free kation will usually come from the adsorbed kations and consist almost entirely of the simple hydrated ions in most of the cases with which we are concerned.

Only when the micellar fluid has attained nearly to the composition of a definite basic salt will the concentration of basic kations be such that any considerable number of these can escape into the intermicellar solution. These conditions are most likely to arise when the sol has a high concentration of free kations in the intermicellar fluid and a low value for the ratio, micellar hydroxide/bound kation.

When the micelle has reached this condition it can be considered to be a liquid or glassy basic salt. This may either persist as a very clear transparent sol for a long time, or it may break up and pass into true solution, or it may actually crystallise. Such crystalline basic salts will only be easily attainable if they are sparingly soluble and have good crystallising powers, and if the tendency for the metal hydroxide to co-ordinate to the kation is high.

The only certain case in which a definite crystalline basic chloride has been observed to crystallise directly from a metal hydroxide sol is that of thorium hydroxide sol No. 10 which, after 6 years, had deposited a small amount of the *compound* $3Th(OH)_4,ThCl_4,10H_2O$, probably $[Th\{Th(OH)_4\}_3]Cl_4,10H_2O$. No such basic thorium chloride is recorded in the literature, though Rosenheim and Schilling (*Ber.*, 1900, **33**, 978), Rosenheim, Samter, and Davidsohn (*Z. anorg. Chem.*, 1903, **35**, 425), and Matignon and Delépine (*Ann. Chim. Phys.*, 1907, **10**, 133) have prepared $Th(OH)_4,ThCl_4,xH_2O$ and $Th(OH)_4,3ThCl_4,xH_2O$ with various values of x, in a crystalline state. There are also indications that crystalline basic chlorides can separate from sols of lanthanum and neodymium hydroxides (see pp. 299, 300).

When hydrion becomes bound to the hydroxide micelle some of it will also dissolve in the micellar fluid. There it may react at once with the hydroxide to form kations of the metal, which will then react as outlined above. In such cases, sols prepared by peptisation with hydrochloric acid will be indistinguishable from those of similar concentration peptised by metal chloride. This is true of sols prepared from translucent aluminium hydroxide precipitated and washed at room temperature.

If, for any reason, the hydroxide does not react easily with hydrion, the latter may persist for a considerable time and the hydrion dissolved in the two liquid phases will be in equilibrium *via* the hydrion adsorbed on the outside of the micellar "droplets." In such a case the sols prepared by peptisation with hydrochloric acid will differ from those peptised by the metal chloride, though in time they should become identical. Sols derived from translucent aluminium hydroxide prepared at 100° behaved in this manner (see p. 289). This hydroxide may be regarded as based on Al_2O_3,H_2O (cf. Böhm, *Z. anorg. Chem.*, 1925, **149**, 203).

Crystalline basic aluminium sulphates isolated *via* the sols as indicated above appear to contain ions in which the aluminium ion is co-ordinated to hydroxide. (Confirmation of this by *X*-ray examination of the crystals is still required.) It is probably basic ions of this type which will be chiefly formed from hydroxides of tervalent metals under sol conditions where the hydroxide is always in relative excess. Under other conditions, as we know from work not yet published, simple hydroxylated ions such as $[AlOH(H_2O)_5]^{\cdot\cdot}$ may occur. We have observed no indication that simple basic kations of this type play any important part in metal hydroxide sols such as we have studied. Such evidence as

we have is rather against it, for a large proportion of the total aluminium which was not obtained as crystalline compounds containing the very basic kations described above has been isolated as ammonium alum.

Additional evidence for our emulsoid theory is furnished by the chromium hydroxide sols where, in several cases, curious glassy products were obtained during the preparation of the sols which were very insoluble in water and approximated in composition to a basic salt, $[Cr\{Cr(OH)_3\}_6]Cl_3,xH_2O$.

The tendency for the aluminium basic micelles to pass into true solution seems to be much greater than that of the corresponding micelles of the other hydroxides, which tend therefore to remain in the emulsoid or glassy condition. If sufficiently favourable conditions for crystallisation could be found, it should be possible to prepare crystalline basic salts from all the sols examined by us.

The emulsoid theory also gives a satisfactory explanation of the limiting value of the ratio, metal hydroxide/bound kations (called "*n*" in the tables), which is strongly indicated in the case of ferric and chromium sols. It is evidently due to the formation of ions similar to those found with aluminium. An *n* value of 4 or 6 for chromium would correspond to the ions $[Cr\{Cr(OH)_3\}_4]^{\cdots}$ and $[Cr\{Cr(OH)_3\}_6]^{\cdots}$. If such low *n* values were determined entirely by adsorption on the surface of solid particles, these would have to be so small that they would be of "molecular" dimensions, and micelles of this character might be expected to give rise to crystalloidal rather than colloidal solutions. This applies with still greater force to thorium and other hydroxide sols with an *n* value as low as 2. With aluminium, lanthanum, and thorium hydroxide sols the analytical figures appear to show that *n* values even lower than 2 may occur. The same is true of the ferric sols prepared by the action of boiling water on ferric chloride. It is possible that in certain cases very low *n* values may arise because so many hydrated kations (*e.g.*, $[Al(H_2O)_6]^{\cdots}$) have penetrated into the micellar "fluid" that some have to remain in the hydrated condition, as there is insufficient hydroxide to convert all into basic kations.

All these hydroxide sols give glassy residues on evaporation at room temperature, and the curds obtained by the action of ammonium sulphate break up into angular glassy fragments even in presence of water. Sometimes these fragments are under such strain that they show double refraction.

Work in the basic region of the system Al_2O_3–SO_3–H_2O, not yet published, has, moreover, shown that over a considerable part of the system, two liquid phases coexist. These separate from clear solutions which there is no reason to regard as colloidal, and whereas the one is an ordinary aqueous solution, the other forms transparent spheres and discs of glass which may be relatively large when seen in a microscope. The range of composition of these glasses covers that of the sol micelles under discussion, and like the micelles, they are metastable towards several crystalline basic sulphates, including those described in the present paper.

There is thus much evidence to justify the view that the micelles of hydroxide sols and the curds obtained from them by the action of appropriate anions are of a liquid or glassy nature.

The view that aluminium and other metal hydroxide precipitates are curded emulsions gives a reasonable explanation of the obstinate retention of anions by such precipitates. Retention of anions by microcrystalline hydroxides such as that of aluminium precipitated in the opaque form by means of ammonia in excess is not to be expected and does not in fact occur (see p. 288). Aluminium hydroxide sols can be prepared from the microcrystalline hydroxide formed at room temperature (see p. 287), but we believe that this is impossible unless a proportion of the amorphous hydroxide is present or is formed during peptisation. In the milky sols so obtained, the micelles probably consist of a core of crystalline material protected by an emulsoid sheath of amorphous hydroxide.

We have found that with freshly prepared metal hydroxide sols practically the whole of the chloride is in the filtrate separated from the hydroxide curd after precipitation and washing with ammonia. As some of the sols age, a proportion of the chloride becomes held in the micelle in such a way that it escapes the action of ammonia, and in some cases the amount thus hidden is considerable. Pauli and Valkó (*op. cit.*, p. 520) found that a large proportion of the total chlorion might fail to respond to the calomel electrode, and considered it to be present in some sort of Werner complex. This is quite likely with some of the hydroxides. We consider that these facts are quite consistent with the emulsoid theory.

The ion $[CrCl(H_2O)_5]^{\cdots}$ is well known, and it is possible that a similar aluminium ion may be capable of existence, but, just as there seems no evidence that the simple hydroxylated ion $[Al(OH)(H_2O)_5]^{\cdots}$ is of importance in sols under ordinary conditions, so there is no evidence for the presence of $[AlCl(H_2O)_5]^{\cdots}$ or any other chlorinated ion: there is, in fact, strong evidence to the contrary. It was found that one of the crystalline basic salts would dissolve in 0·1N-hydrochloric acid, and if the solution was then diluted 2½ times a considerable fraction of the solute crystallised out again unchanged, containing no trace of chlorine (see p. 291). This unexpected behaviour indicates a high degree of stability of the basic aluminium ions and is strongly opposed to the view that any replacement of their hydroxyl by

chlorine is likely to occur. It is evident that simple hydroxylated or chlorinated kations of aluminium, chromium, or other metals could take part in the adsorption equilibria like any other kation if they were prepared by suitable methods and added to the hydroxide sols. That does not mean, however, that they are normally present in appreciable amount in such sols prepared by peptisation in the usual way.

Masking of chlorion owing to retention in the liquid or glassy micelle must not be confused with another effect. All negative ions present in the system take some part in the precipitation whenever a positive sol is curded by sufficient addition of suitable electrolytes. All the curds obtained from our sols by the action of ammonia would be expected to carry down a little chloride for this reason, but it would be removed relatively easily by washing with ammonia, though not by water. Action of this sort is not likely to be very important in the case of chlorion, since the efficacy of anions as coagulants is mainly determined by their valency and tendency to form sparingly soluble salts.

It is evident that, for all the reasons discussed, there must be considerable uncertainty about the micellar charge. This is likely to be greatest in old sols. Sol analyses in which chlorion concentrations have been determined by means of the calomel electrode are not necessarily any more correct than those obtained by our chemical methods. A knowledge of the free kations present is essential—it cannot be assumed that only free negative ions are present in a positive sol in addition to the positive micelles.

Nearly all the sols with which we have worked were prepared by peptisation of the metal hydroxide in a solution of the corresponding chloride or by hydrochloric acid. The former peptising agent may be the more effective, and sols prepared by the two methods are not always identical (see p. 280). They were fairly concentrated and were not subjected to dialysis, which would have rendered them less suitable for our purpose. The free metal ion was estimated in the filtrates from gels obtained with ammonium sulphate in the case of all the sols except those of chromium hydroxide, which were coagulated by potassium ferrocyanide. Total chloride was determined in the filtrate from the curd obtained with excess of ammonia, the curd being well washed with ammonia. Alternatively, the sol was digested under reflux well below 100° with 2N-nitric acid until the colloidal condition was broken down, and chloride was then determined in the solution by means of silver nitrate. Results obtained by these two methods usually agreed closely. Hydrion present in the sols could only be determined with certainty by means of the glass electrode in the case of aluminium, ferric, and chromium sols, although the chemical method was satisfactory for thorium sols (see pp. 278, 300). "Total chloride" less "free metal ion and hydrion" gave "bound metal ion."

The analytical difficulties are considerable and the differences sought are often small, but the following conclusions seem to be justified by the results obtained.

Period required for Peptisation at Room Temperature.—The rate of sol formation increases with the concentration and the excess of peptising agent employed, provided that the amount of hydroxide present be not enough to act as a mechanical barrier to liquid motion; for instance, compressed cakes of ferric or chromium hydroxide are difficult to disperse by limited volumes of liquid. This effect is of importance when preparing very concentrated sols. The actual time before peptisation is complete varies widely from case to case—many days may be needed. The curding effect of a high concentration of peptising agent may interfere with sol formation.

The *rate of ageing* of the sols as indicated by the setting free of previously bound kations is always slow. It appears to be more rapid in the aluminium and ferric sols than in the others examined by us.

Hydrolysis of Sols and the Part played by Hydrions.—No hydrolysis was apparent in any hydroxide sol of lanthanum or neodymium. The glass electrode showed that the p_H was about 7·5. Very little acid was present in the chromium and the thorium sols, but the aluminium and ferric sols contained an appreciable amount. These differences are connected with the different degrees of hydrolysis of the several metal chlorides. Pauli and Valkó (*op. cit.*, p. 100) suggested that, on adsorption by a metal hydroxide, hydrions would probably react with hydroxyl to form water and so liberate an equivalent amount of metal ion. The nature of the metal and other circumstances will, however, determine whether this happens. It is quite possible for a hydrion to remain in close proximity with a hydroxyl group covalently attached to a metal atom (which is not the same as a hydroxyl ion), just as it can remain associated with a water molecule: the less electropositive the metal the more readily this will happen. It seems clear that hydrolytic equilibria of the types

$$[Al(H_2O)_6]^{\cdots} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{\cdot\cdot} + [H^{\cdot},H_2O]$$
$$[Al(OH)(H_2O)_5]^{\cdot\cdot} + H_2O \rightleftharpoons [Al(OH)_2(H_2O)_4]^{\cdot} + [H^{\cdot},H_2O]$$
$$[Al(OH)_2(H_2O)_4]^{\cdot} \rightleftharpoons Al(OH)_3 + [H^{\cdot},H_2O] + H_2O$$

must occur in the solution. All the ions so formed will be adsorbed on and dissolve in the micelles of the sol to some extent. In so far as their adsorption is determined by dipole effects, it will depend

upon the charge and volume of the adsorbed ion and might be expected to diminish in the order $[H^{\cdot},H_2O] > [Al(H_2O)_6]^{\cdot\cdot\cdot} > [Al(OH)(H_2O)_5]^{\cdot\cdot} > [Al(OH)_2(H_2O)_4]^{\cdot}$.

It is important to recognise that the whole series of ions consisting of $[Al(H_2O)_6]^{\cdot\cdot\cdot}$ at one end and $[H^{\cdot},H_2O]$ and neutral $[Al(OH)_3]$ at the other, with all possible basic ions as intermediate stages, must co-exist in approximate hydrolytic equilibrium in the intermicellar and micellar liquids and in the adsorption film. It is convenient to consider aluminium sols as an example, for the various possible ions are better known to us than those of other metals.

The proportions of the various members of this series which are present in different sols will depend upon several factors of which the chief will be (*a*) the specific peculiarities of the metal, (*b*) the concentration of the sol and in particular that of the " free " kation, and (*c*) the *n* value of the sol. The lower the value of *n*, the more will basic ions of the highest basicity be favoured, whereas a high concentration of total free kations in a sol will tend to favour the simpler kations rather than the basic ions.

The equilibria concerned will not be absolute, for the sol condition is a metastable one and, in the sols under consideration, represents a transition stage leading from amorphous hydroxide to crystalline hydroxide or crystalline basic salt.

The precise ionic state of a sol is hard to define and depends upon its past history—whether it has been freshly prepared and by what method, whether it has been dialysed, and so forth.

The two chief causes of the increase of free kations when emulsoid sols age would seem to be: (1) diminution of surface owing to coalescence of emulsoid droplets and consequent liberation of some of the adsorbed kations, (2) adjustment of the hydrolytic equilibria owing to increased formation of basic ions. This does not necessarily increase the number of positive equivalent ions in solution, but does increase the total amount of metal in the " free " state in solution.

It would appear that a peculiar situation might arise when the micelles of a sol, having become saturated with kations, break up and pass into true solution as very basic kations. Before this occurrence, the various kations present in the intermicellar fluid would be in approximate hydrolytic equilibrium. This would be upset by the sudden influx of very basic kations, and one of two things would probably happen: either the very basic kations would separate out as crystalline basic salts or, if solubility conditions were not suitable for this, fresh readjustments of the hydrolytic equilibria would occur. These might lead either to an increase of simpler basic kations at the expense of non-basic kations or to an actual separation of metal hydroxide, and as this would probably be slow, the conditions should be very suitable for formation of crystalline hydroxide or oxide.

A change in the proportions of hydrion and metal ions in the intermicellar fluid may arise owing to a change in the nature of the micelle due to dehydration, or to some other cause accompanied by a change in the relative adsorptive capacity of its surface for these ions. This seems to apply to ferric sols. Owing to their positions in the adsorption scale it would seem that with most hydroxide sols the simple hydrated metal ions are probably the principal stabilising ions, with the various basic ions playing minor parts. Hydrion may become important as a stabilising ion with the more acidic or less reactive hydroxides (see p. 300 for a case with thorium hydroxide, and p. 289 for two examples with aluminium hydroxide).

The series of hydrolytic equilibria mentioned above may come into action in a solution prepared from a simple metallic salt. This happens with ferric chloride. A freshly prepared, dilute (0·5N) solution of this salt in cold water rapidly reaches a condition of apparent hydrolytic equilibrium with a low hydrion concentration. A slow hydrolysis continues, however, and after several years practically the whole iron content of the original solution may have separated as a yellow precipitate below a colourless solution of hydrochloric acid. The hydrolytic changes seem to be accentuated in this case by the formation of the less basic or less reactive Fe_2O_3,H_2O, which forms in ageing sols.

Freshly prepared ferric hydroxide sols, if sufficiently concentrated, can give a precipitate with hydrochloric acid. The less concentrated sols give none in the fresh condition but, as they age, they give a yellow precipitate with hydrochloric (or nitric) acid in increasing amount, until when they are a year old, over 80% of the iron content may be precipitated. These yellow precipitates are again dispersed by addition of water. Analysis of such a precipitate, thrown down by 2N-hydrochloric acid from a four-year old ferric hydroxide sol, washed with alcohol, and dried in air, gave figures corresponding to $(FeO,OH)_{10\cdot7},[Fe(OH)_3]_3,FeCl_3$, whereas ferric hydroxide, precipitated cold and similarly washed and dried, was $Fe(OH)_3,0{\cdot}74H_2O$. The alcohol washing of the curd had removed some ferric chloride,* so the precise formula is uncertain, but the result suggests that the ageing process producing the less soluble curd is a partial dehydration of the original micelle which, in the fully aged sol, would presumably be based upon FeO·OH instead of $Fe(OH)_3$ (cf. Böhm, *loc. cit.*). These changes

* Much more than could have been present in the small amount of adhering mother-liquor. This supports the view that bound ferric ions, or other kations which could readily react to give ferric ions, were present on the curd.

are accompanied by a small but distinct increase in the acidity of the sol, and after several years a considerable amount of the iron content may have separated out as a yellow curd.

A small increase with age in the n value of the sol may be a contributory cause of the decreasing solubility of the curd, but seems insufficient by itself to account for the observed behaviour. The different behaviour of thorium hydroxide sols prepared by the hot and the cold processes may also be due to a difference in the degree of hydration of the micelles.

A considerable orange-brown deposit had settled out of ferric hydroxide sol No. 25 (see p. 297) by the time this was $3\frac{3}{4}$ years old. This was still colloidal and easily dispersed by water, but its X-ray powder photograph appeared to be identical with that given by Böhm (*loc. cit.*) for the mineral rubinglimmer (ruby mica, γ-goethite), the form of Fe_2O_3,H_2O corresponding to bauxite, γ-Al_2O_3,H_2O. (Böhm showed that bauxite is not $Al_2O_3,2H_2O$, as commonly stated.) It seems evident, therefore, that the majority of ferric hydroxide sols prepared by the cold process will eventually deposit crystalline γ-Fe_2O_3,H_2O on ageing. Sols prepared by the hot process will ultimately behave in the same way and so even will solutions of ferric chloride. The reversal of the hydrolysis which the hot-process sols appear to show on ageing at room temperature (see p. 295) is to be regared as a metastable interlude only possible so long as crystalline nuclei of the very insoluble γ-Fe_2O_3,H_2O have not formed to an extent sufficient to switch over the hydrolysis in the other direction.

The equilibria in the adsorption film on the micelles and the ionic interchange between the adsorption film and the body of the intermicellar and micellar solutions would seem to be chiefly responsible for the ageing of sols. Colloidal solutions must be regarded as metastable systems. The adsorbed ions, although essential to the very existence of the colloidal state, also provide the mechanism by which this is finally broken down. This matter was discussed in connection with colloidal sulphur by Bassett and Durrant (J., 1931, 2924). The metastability of colloidal systems arises from several causes which will be briefly considered.

(i) The free ions functioning in a sol may be, and generally are, of the wrong kind at first; for instance, hydrion or $[Al(H_2O)_6]^{\cdots}$ in the peptising solution may have to be converted mainly into some basic ion. If such an adjustment occurs slowly, there may well be an initial peptisation and sol formation conditioned by adsorption of ions which slowly undergo adjustment to others more truly characteristic of the particular sol in its more or less stable form. If the adjustment is rapid, it will not be possible to distinguish this from the peptisation stage itself. Slowness in the rate at which the minimum concentration of free kations was reached in some of our experiments may be due to some such cause.

(ii) If a sol is an emulsoid, there will usually be an instability due to a tendency towards diminution of micellar surface by formation of larger " droplets " and ultimately of an uncharged, second, liquid phase. This is probably one of the causes of the normal slow separation of kations from these sols on ageing, for diminished surface means diminished adsorption.

(iii) In metal hydroxide sols, instability may arise owing to a tendency for the hydroxide to lose water. Our evidence suggests that the ageing of ferric hydroxide sols is connected with the slow formation of FeO·OH from $Fe(OH)_3$. The existence of basic salts derived from both forms of the hydroxide should be possible. There is no apparent reason why the " liquid " micelles should not persist after this change has occurred though their capacity for being " curded " will be different.

(iv) Separation of a definite crystalline compound from the sol (or formation of its crystalloid solution) is another very important cause of instability. The type of crystalline compound which can separate from any given type of sol may well depend upon several factors such as concentration of sol, proportion of free and bound kations, and temperature. For example, with aluminium hydroxide sols there would seem to be the possibility of the sols being metastable towards one of several definite crystalline basic salts or towards either of the crystalline hydroxides $Al_2O_3,3H_2O$ or Al_2O_3,H_2O in either of the two forms in which these compounds occur. The tendency for such compounds to form or to crystallise varies widely with different metals, so the rate at which metal hydroxide sols change and age may be expected to vary greatly. Relatively stable sols can only be expected in those cases where there is a very small tendency to crystallise on the part of the compounds which might separate. Solubility is important in this connection. The case might arise of a sol which could be metastable towards more than one crystalline compound. The rate of ageing in such a sol would vary according to which particular compound was tending to separate.

Most of these changes are very slow and do not lead to macroscopic crystals except over long periods of time. Even the microcrystalline material which is formed and is identifiable by means of X-rays may have a very imperfect lattice. It may still even be partly colloidal, in the sense that it may contain considerable portions of strongly adsorbing non-crystalline material. As the micelles of a sol become more crystalline and less adsorbing, their " solubility " gets less until finally the prevailing concentration of the oppositely charged (or " gegen ") ions is able to cause flocculation (cf. Bassett and

Durrant, *loc. cit.*, pp. 2927—2933). The precipitate which slowly separates from many sols is, for this reason, to be regarded as being a partly crystalline gel. The case has some similarity to that of the formation of graphite from coke considered by Riley (*Chem. and Ind.*, 1939, **58**, 391).

Preparation of Crystalline Basic Aluminium Sulphates.—The observation that certain basic aluminium sulphates are well crystallised and sparingly soluble in water has enabled information of value to be obtained about the nature and conditions of the basic ions formed in aluminium hydroxide sols. The experimental evidence is given on pp. 290, 293. These compounds can be obtained by several methods *via* sols prepared as follows so as to have the basicity of the compound desired: (1) by peptisation of aluminium hydroxide (precipitated from boiling solution) with aluminium chloride, but not with hydrochloric acid; (2) by peptisation of aluminium hydroxide (precipitated at room temperature in the translucent form) with either aluminium chloride or hydrochloric acid; (3) by adding the calculated amount of ammonia, slowly and with constant stirring, to a solution of aluminium chloride. The last is the best and simplest method of preparation, for it avoids the tedious filtration and washing of the precipitated hydroxide. The precipitate first formed rapidly redissolves owing to peptisation and a faintly turbid solution is obtained. This is a true sol, nevertheless, and if it is treated at once with a solution of ammonium sulphate a typical amorphous curd is precipitated. Sooner or later the sol breaks down, so that if some time elapses before addition of the sulphate, the precipitate obtained may be either partly or entirely crystalline.

The spontaneous breakdown of the sol at room temperature is uncertain, however, but if the sol is boiled for a short time it becomes absolutely clear and then gives an entirely crystalline precipitate on treatment with ammonium sulphate. The crystalline basic salts can be easily separated from any coprecipitated amorphous curd by treatment with a little dilute hydrochloric acid before filtration. This dissolves the latter without affecting the former.

From the details given for the preparation of basic aluminium sulphates, it is clear that basic salts and ions must play an important part in metal hydroxide sols. A complete study of all the compounds involved would be very prolonged and only a beginning has been made with the aluminium compounds isolated in the form of sulphates. The number of these salts which exist is evidently large and only provisional statements as to their formulæ, etc., can yet be made. The information now available suggests that at least four very basic aluminium sulphates can be obtained. Those with molecular ratios $Al_2O_3/SO_3 = 1{\cdot}67$, 1·71, and 2·17, and another with a ratio which is probably 2·0 give distinct *X*-ray powder diagrams suggestive of chemical individuality; their general crystallographic appearance and other characteristics also support this view. Several basic sulphates with very low Al_2O_3/SO_3 ratios are already known from other work, not yet published, but these are not considered now. The preparative data given make it probable, however, that there also exist other basic sulphates with Al_2O_3/SO_3 ratios below 1·67 and there is probably a number between the salt with this ratio and aluminium sulphate (ratio 0·33). It is hoped that determinations of the structures of all these compounds will be possible by *X*-ray methods. Various structures could be suggested, but for each of the four *compounds* indicated above one is given which is not incompatible with data for cell weights deduced from *X*-ray powder diagrams:

$[Al\{Al(OH)_3\}_4]_2[SO_4]_3[H_2O]_{17 \text{ or } 18}$	$Al_2O_3/SO_3 = 1{\cdot}67.$
$[Al(OH)\{Al(OH)_3\}_3][Al\{Al(OH)_3\}_4]_4[SO_4]_7[H_2O]_{32 \text{ or } 33}$	$Al_2O_3/SO_3 = 1{\cdot}714.$
$[Al(H_2O)\{Al(OH)_3\}_5][Al\{Al(OH_3\}_6][SO_4]_3[H_2O]_{20\text{-}5 \text{ or } 21}$	$Al_2O_3/SO_3 = 2{\cdot}17.$
$[Al(H_2O)\{Al(OH)_3\}_5]_2[SO_4]_3$	$Al_2O_3/SO_3 = 2{\cdot}00.$

The last is included because the *X*-ray powder diagram of a preparation with $Al_2O_3/SO_3 = 1{\cdot}90$ was distinctive and did not correspond to a mixture of the other three basic sulphates.

Experimental.

Preparation of Sols (see p. 282).—The hydroxides required were prepared by the action of excess of ammonia, generally in the cold, on a solution of the chloride, and were well washed, first with dilute ammonia and then with cold water. The ammonia washing is essential with lanthanum and neodymium hydroxides, for otherwise autopeptisation occurs when all but a small amount of the chloride has been removed. The washed hydroxide was thoroughly mixed by means of a spatula or pestle into the hydrochloric acid or metal chloride solution used for peptisation. By using solutions of suitable concentrations and allowing for the water and any chlorion (see p. 281) in the wet hydroxide, it was possible to prepare sols of concentrations and metal hydroxide/metal chloride ratios which were very close to those intended.

Appearance of the Sols.—Lanthanum and aluminium hydroxide sols are translucent or milky, though the latter may be quite clear and transparent; the neodymium hydroxide sols are translucent, blue by reflected, reddish by transmitted, light. [The most concentrated neodymium sol prepared was only 0·23N with respect to $Nd(OH)_3$.]

Thorium hydroxide sols prepared by boiling are clear and transparent, whereas more concentrated ones, prepared in the cold, may be clear and transparent or translucent; if well below N with respect to $Th(OH)_4$, they remain transparent for years. They show the Tyndall beam. The ferric and chromium hydroxide sols are reddish-brown and green, respectively, and clear and transparent, but show a Tyndall beam. The ferric sols gradually become yellower and less transparent with age and slightly turbid, and the chromium sols very slowly become less transparent.

Thixotropy was very marked in the aluminium sols and in the most concentrated lanthanum sols. All the sols considered in this paper give glass-like residues on evaporation at room temperature over sulphuric acid. These redissolve in water.

Analysis of Sols.—2, 5, 10, or 20 C.c. were used for analysis according to the concentration.

Total metal and total chloride. The sol is boiled with a considerable excess of ammonia, and the precipitate washed with hot dilute ammonia till free from chloride; it is then ignited and weighed as oxide. The estimation of total metal in lanthanum or neodymium hydroxide sols is best done by curding it with a small excess of ammonium oxalate, igniting the washed curd, and weighing as oxide.

The filtrate from the hydroxide or oxalate precipitate is acidified with nitric acid, and the chloride precipitated and weighed as silver chloride. Alternatively, the chloride is determined in a separate portion of the sol after digestion with nitric acid. The extent to which results obtained by the two methods may differ is shown on p. 287.

" Free " metal ion. The sol is curded with a solution of a suitable salt added with shaking from a burette. In some cases it is better not to wash the curd, but the volume of filtrate is determined, compared with the volume before filtration, and the necessary allowance made. Lanthanum or neodymium is precipitated from the filtrate and washings as oxalate, the other metals as hydroxide by ammonia. The precipitate is filtered off, washed, ignited, and weighed as oxide.

Ammonium sulphate is the best coagulant for all the sols except those of chromium hydroxide, which it does not precipitate completely. Excess of the sulphate may be used without danger in most cases, but separation of sparingly soluble, crystalline, basic sulphates may occasionally lead to errors. Such separation may be almost entirely avoided by using the minimum amount of a dilute solution of the ammonium salt. Microscopic examination of the curd will show whether any crystals of basic salt have separated. Only a slight excess of ammonium sulphate should be employed with lanthanum and neodymium sols, for excess tends to dissolve the precipitate, and it is best not to wash this. Potassium ferrocyanide is used to curd the chromium hydroxide sols, since it precipitates the micelles quantitatively when added in amounts equivalent to the " bound " chromium ions and does not precipitate " free " chromium ions. The ferrocyanide curd must be well washed with water. The potassium ferrocyanide solution should be freshly prepared with boiled-out water, for otherwise a little alkali may be present owing to oxidation to ferricyanide: this alkali might precipitate some of the free metal ion along with the micelles. The ferrocyanide should be added until no further curd is produced—a point not always easy to determine—for excess should be reduced to a minimum. Any such excess is carried down by the chromium hydroxide when this is subsequently precipitated by boiling the filtrate from the curd with ammonia, and after ignition the chromium sesquioxide is contaminated with ferric oxide, leading to high results for free $Cr^{\cdots}$. Ferrocyanide can be used similarly for the aluminium sols, as it does not precipitate free aluminium ions; ammonium sulphate is preferable, however.

The results given in the tables are expressed in mg.-equivs./l. Those for total metal, " free " metal ion, and total chloride were determined directly, whereas the figures for " bound " metal ion were obtained by deducting (" free " metal ion + $H^{\cdot}$) from total chloride, and the figures for " un-ionised " metal (in the micelles) by deducting (" bound " + " free " metal ions) from " total " metal. The ratio n has been defined on p. 281.

Hydrion recorded in the tables for thorium and chromium hydroxide sols was determined by titration of the filtrate from curds produced by the minimum amount of metaphosphate. Glass-electrode determinations with the thorium hydroxide sols and the diluted chromium hydroxide sol 3 show that the determinations by the titration method are probably fairly accurate.

" Bound " metal ion includes that present as complex basic ions in solution in the micelles as well as hydrated or basic kations adsorbed on the surface of the micelles (see p. 280). " Free " metal ion includes all metal recovered from the curd filtrate, part of which in some cases may have been present as basic ions. " Un-ionised " metal includes that of metal hydroxide co-ordinated to metal ions in the micelles and in some cases consists almost entirely of this.

Masking of Chloride in Old Sols (see p. 281).

$La(OH)_3$, sol 9.

	Composition, mg.-equivs./l.		
Age of sol, days.	La.	Cl (after curding sol with ammonium oxalate and washing precipitate).	Cl (after destruction of sol with HNO_3).
3	1049	157·6	159·1
143	1049	151·2	159·4

$Fe(OH)_3$, sol 27. The nitric acid method is very troublesome with old ferric and aluminium hydroxide

sols, for the curd produced can only be dissolved with great difficulty and care has to be taken not to lose chlorine during the operation.

	Composition, mg.-equivs./l.		
Age of sol, days.	Fe.	Cl (after curding sol and washing precipitate with ammonia).	Cl (after destruction of sol with HNO_3).
3	509·7	61·4	—
58	509·7	58·4	61·6

$Al(OH)_3$, sol 3.			
Age, days.	Al.	Cl (by ammonia method).	Cl (by HNO_3 method).
1785	1242	184	186

A similar result was obtained with another aluminium hydroxide sol 860 days old.

Aluminium Hydroxide Sols.

When aluminium hydroxide is precipitated from boiling solution, it is translucent and is essentially Al_2O_3,H_2O (Böhm, *loc. cit.*). It can be filtered off and washed comparatively easily and can be peptised readily by either hydrochloric acid or aluminium chloride to give translucent sols. A translucent precipitate is obtained also at room temperature if the minimum amount of ammonia is used, but it is filtered off and washed only with extreme slowness.

When a large excess of ammonia is used in the precipitation at room temperature a white opaque hydroxide is obtained which is easily filtered off and washed, but some aluminium remains in solution. With smaller excess of ammonia, the translucent precipitate, on standing in contact with the ammonia, becomes white and opaque in from less than an hour to many hours according to the excess of ammonia employed. This precipitate gives an *X*-ray diagram characteristic of a microcrystalline solid but not of hydrargillite (gibbsite), the ordinary form of crystalline $Al_2O_3,3H_2O$. The diagram is identical with that of a preparation obtained and described by Böhm (*loc. cit.*, p. 208), who appears to have considered that it was a second form of $Al_2O_3,3H_2O$. We are of the same opinion, and have obtained a solid giving the same *X*-ray diagram by floating a solution of aluminium sulphate upon a concentrated solution of sodium aluminate. The precipitate formed at the junction of the two solutions was separated and well washed after 2 months.

One preparation of the microcrystalline hydroxide was obtained by adding 100 c.c. of approx. 8N-ammonia to 8 g. of aluminium chloride hexahydrate in 100 c.c. of water and leaving the mixture in a closed vessel for a month before filtration and thorough washing with cold water. After drying over concentrated sulphuric acid the water content was 35·3% (calc. for $Al_2O_3,3H_2O$: H_2O, 34·6%). The air-dried material contained H_2O, 35·7%, but this depends largely on the conditions of precipitation. Another sample, in the preparation of which a much smaller excess of more dilute ammonia had been used, contained H_2O, 44·5%.

The *X*-ray diagram of the fully dried compound (H_2O, 35·3%) was identical with that of the preparation which approximated to $Al_2O_3,4{\cdot}5H_2O$ and contained H_2O, 44·5%, so it is clear that no higher hydrate than $Al_2O_3,3H_2O$ is involved.

The whole of the aluminium can be precipitated in the cold from concentrated solutions of the chloride by approximately five-sixths of the ammonia theoretically needed to produce the hydroxide. The precipitate can be regarded either as a basic salt or, as we consider, a gel in which the curding has been produced partly by hydroxyl ions and partly by chlorions. The proportion of the latter present depends upon the dilution of the initial solution, and some of it will be in solution in the micellar fluid. Most of the chlorion is easily replaceable by hydroxyl if more ammonia is added.

The translucent precipitate obtained in the cold is very reactive and is readily peptised by either hydrochloric acid or aluminium chloride to give translucent sols. The opaque, microcrystalline hydroxide is much less reactive, and although milky, opaque sols can be obtained from it by peptisation with either of the agents just mentioned, its behaviour is somewhat uncertain. It does not appear possible to peptise some samples, and the majority of those which can be peptised contain a portion which settles out very easily from the sols produced. We believe that peptisation is usually dependent upon the presence of a proportion of the amorphous material which acts as a protective colloid, so that the micelles of the sol produced contain a microcrystalline core with an emulsoid sheath formed from the amorphous material.

Two portions of the opaque, microcrystalline hydroxide from approx. 3·3 g. of the hexahydrated chloride (the *X*-ray diagram of which suggested freedom from amorphous material) were treated, one with 1·5 g. of the hexahydrate in 9 c.c. of water, and the other with the equivalent amount (9 c.c.) of 2N-hydrochloric acid. The former had given after 12 days a good, milky, opaque, thixotropic sol with no apparent sediment, but the latter did not give a sol in spite of occasional shaking for 6 days; a further shake then gave a good sol indistinguishable by eye from the other. If the hydroxide contained some of the amorphous form, a thin film of basic salt could be expected to form easily in the solution containing $[Al(H_2O)_6]^{\cdots}$ ions, but with greater difficulty in the acid solution. Addition of 10 c.c. of water after 5 days to the second sol caused it to "break" and a milky sol never re-formed. The other sol also broke spontaneously later and did not re-form.

It seems likely that this spontaneous "breaking" of the sols occurs when the emulsoid sheath either becomes detached from the micelles or, having become saturated with kations, passes into true solution as

basic kations. The experiments on the preparation of very basic sulphates (pp. 290, 293) show that, sooner or later, this will occur. The microcrystalline aluminium hydroxide particles after losing their protective sheaths will settle out as a normal precipitate. The liquid above this precipitate was still a sol, though only faintly turbid. With a small amount of ammonium sulphate it gave an amorphous curd, and the filtrate from this, with much more ammonium sulphate, gave an abundant deposit of small octahedra of ammonium alum. The solution from the sol which had been peptised by aluminium chloride gave more of the amorphous curd than did that from the sol peptised by hydrochloric acid. Conditions in both mixtures were evidently essentially similar to those prevailing in aluminium hydroxide sol No. 9 (Table I) which were studied in much more detail.

Proportion of Sulphate carried down by Different Varieties of Precipitated Aluminium Hydroxide.—Aluminium hydroxide was precipitated from solutions containing known amounts of pure aluminium sulphate in four different ways: (*a*), in the cold, only sufficient ammonia being used to give a mixture alkaline to litmus; (*b*) and (*c*), from boiling solution, about twice and ten times the theoretical amount of ammonia being used, respectively; (*d*), in the cold with a large excess of ammonia. The several precipitates were then thoroughly washed until apparently free from sulphate, cold water being used for preparations (*a*) and (*d*), hot water for (*b*), and hot dilute ammonia followed by hot water for (*c*). The washed precipitates were then dissolved in hydrochloric acid, and the sulphate present estimated as barium sulphate. Precipitate (*a*) had retained 6·13% of the total SO_3, whence $Al_2O_3/SO_3 = 5{\cdot}44$. This low value is not surprising, since the ammonia used to form the precipitate was less than that theoretically required for pure hydroxide: it must be regarded as consisting in part at least of basic salt. Preparation (*b*) had retained 2·06% of the total SO_3, whence $Al_2O_3/SO_3 = 16{\cdot}2$, and (*c*) had retained 0·054% of the total SO_3, whence $Al_2O_3/SO_3 = 613$. The microcrystalline (*d*) precipitate, $Al_2O_3,3H_2O$, had retained 0·2% of the total SO_3; *i.e.*, $Al_2O_3/SO_3 = 163{\cdot}4$: this may be reasonably attributed to surface adsorption. Chloride is less readily adsorbed than sulphate, and a sample of the microcrystalline hydroxide precipitated as in (*d*) but from the chloride instead of the sulphate contained, after thorough washing, only enough chloride to give an atomic ratio Al/Cl = 1634.

Preparation (*c*) gave the *X*-ray powder diagram characteristic of both natural and synthetic bauxite, Al_2O_3,H_2O (Böhm, *loc. cit.*). Preparation (*b*) gave the same diagram, but only the strong lines were visible and they were rather diffuse, while even preparation (*a*) showed the same lines but very diffuse, indicating a partly amorphous condition.

According to this evidence preparation (*c*) was definitely microcrystalline, whereas (*a*) was amorphous with incipient formation of a bauxite lattice, and in (*b*) the bauxite lattice was still further developed. The large proportion of sulphate present in (*a*) and (*b*) did not give rise to any bands in the *X*-ray diagrams which could be attributed to basic sulphates. We have therefore obtained the bauxite form of the monohydrate both at room temperature and near the boiling point of water, whereas the second form of the trihydrate $Al_2O_3,3H_2O$, which we have obtained at room temperature, was first obtained by Böhm at about 100°. It is probably to be regarded as the α-form corresponding to diaspore, α-Al_2O_3,H_2O. Both bauxite and the other form of the trihydrate (hydrargillite or gibbsite) occur in Nature and, according to Haber (*Naturwiss.*, 1925, **13**, 1007), are corresponding γ-forms.

The gel obtained by precipitating an aluminium chloride solution with approximately five-sixths of the ammonia theoretically required to form hydroxide (see p. 287) gave an *X*-ray diagram showing the strong lines of hydrargillite, which were rather diffuse. This indicates that the gel was amorphous with incipient formation of a hydrargillite lattice. The gel thrown down by ammonium sulphate from old aluminium hydroxide sol No. 9 was a mixture of α-$Al_2O_3,3H_2O$ and γ-$Al_2O_3,3H_2O$ (see p. 289).

It would seem that the evidence is insufficient for any conclusions to be drawn regarding the relative stabilities of $Al_2O_3,3H_2O$ and Al_2O_3,H_2O at different temperatures.

No satisfactory neutral coagulant for aluminium hydroxide sols has been found which will also precipitate the free aluminium ions. There is thus no titration method for determining their acidity. Only the glass electrode is satisfactory. No glass-electrode measurements were made on the earlier sols, but those made on later ones showed that the hydrion concentration was very small except in sol No. 8—a special case. It is therefore reasonable to assume that the hydrion concentration can usually be neglected in cases where no measurements are available.

The figures for "Free $Al^{\cdots}$" are not easily determined and are subject to an uncertainty of possibly about ± 5 mg.-equivs./l. In spite of this, it appears certain that on ageing both types of sol (*i.e.*, those prepared from hot- and from cold-precipitated hydroxide) there is a slow increase in the concentration of the free aluminium ions present: in some cases this is rapid. There is little indication of the attainment of any preferential value of n such as we have found with other hydroxides.

Table I shows our results for a number of sols. Glass-electrode measurements on sols 8 and 12 indicate that, when the hot-precipitated hydroxide is peptised by hydrochloric acid, a considerable hydrion concentration may persist for some days, though most of the free kations are aluminion ions. This suggests that in these translucent aluminium sols a portion, and perhaps the major portion, of the bound kations are hydrions, and that as the sols age these bound hydrions slowly react with the substrate to form aluminium ions which become free, in part at least. Unfortunately, we cannot distinguish between bound hydrions and bound aluminium ions.

Many of the aluminium hydroxide sols showed thixotropy. This applies to both milky and translucent

TABLE I.

Aluminium hydroxide sols.

Sol.	Total Al.	Un-ionised Al.	Bound Al$^{\cdots}$.	Free Al$^{\cdots}$.	H$^{\cdot}$.	Cl$^{\prime}$.	n.	Age (days).
5	1221	1063	94	64	—	158	11·3	5
	,,	,,	86·2	71·8	—	,,	12·3	11
	,,	,,	84·5	73·5	—	,,	12·5	336
7	780	663·3	77·7	39	—	117	8·5	3
	,,	,,	77·0	39·7	—	,,	8·6	12
	,,	,,	72·6	44·1	—	,,	9·1	21
	,,	,,	71·1	45·6	0·3	,,	9·3	96
8	247	146·1	67·9	33	—	110	2·1	1
	,,	,,	,,	,,	9·1	,,	,,	3
9	625·8	532·6	37·6	55·6	—	93·5	14·2	1
	,,	,,	45·4	47·8	0·3	,,	11·7	3
	,,	,,	36·5	56·7	—	,,	14·6	6
	,,	,,	34·1	59·1	—	,,	15·6	42
	,,	,,	7·0	86·2	0·3	,,	76·1	425
	338·0	244·0	6·9	86·8	,,	91·7	35·4	980
11	1290	1098	120·2	71·8	—	192	9·1	2
	,,	,,	131·8	60·2	—	,,	8·3	13
	,,	,,	129·7	62·3	—	,,	8·5	34
12	1329	?	?	91·4	—	203·9	?	1
	,,	1167·8	61·2	100	42·7	,,	19·1	5
	,,	?	?	113	—	,,	?	7
	,,	,,	?	155	—	,,	?	24
	,,	1125·5	31·5	172	—	,,	35·7	168
	,,	—	—	—	0·4	,,	—	172
13	2131·7	2010	121·7	0	0	121·7	16·5	12
14	2100	1555·6	123·8	420·6	—	544·4	12·6	6
	,,	,,	82·7	461·7	—	,,	18·8	25
15	1510·6	872·5	203·1	(640)435	0·7	638·8	4·3	3
	,,	,,	192·1	(656)446	—	,,	4·5	25
16	2007	1485·3	338·1	(918)183·6	0·2	521·9	4·4	—

Notes to Table I.—The figures given under " bound Al$^{\cdots}$ " include any bound H$^{\cdot}$ that may have been present (see p. 288). Where this is present, the true values for bound Al$^{\cdots}$ would be less, and those for un-ionised Al greater, by the amount of H$^{\cdot}$; n would become (un-ionised Al)/(bound Al$^{\cdots}$ + H$^{\cdot}$) and would have a larger value than appears in the table.

Sol 5 was made from hydroxide precipitated from the chloride at 100° and peptised by cold hydrochloric acid. Sol 7 was made from hydroxide, prepared as for sol 5, added slowly to 0·2N-hydrochloric acid; in calculating n, the hydrion concentration has been taken as 0·3 throughout.

Sol 8 was prepared as follows: 10 c.c. of 2N-hydrochloric acid were ground with a lump of still moist aluminium hydroxide precipitated at 100° which had been stored for 6 months, and the mixture diluted to 30 c.c. and placed in a graduated cylinder; after standing overnight there were a 7·5-c.c. zone of translucent jelly at the bottom of the cylinder, 15 c.c. of practically clear liquid at the top, and a 7·5-c.c. zone, somewhat milky, between the two. Analysis of the upper clear liquid showed that it was a solution of hydrochloric acid and aluminium chloride approx. 0·18N for aluminium and 0·62N for chlorine; 5 c.c. of the jelly from the bottom were shaken with water to yield 30 c.c. of a translucent sol which gave no deposit on standing. This was analysed 1 day after dilution of the jelly.

Sol 9 was prepared from cold-precipitated hydroxide peptised by 0·2N-hydrochloric acid. There was a small deposit from this sol which was shaken before removal of samples for analysis. The amount of this deposit was large in both the 425- and the 980-days old sol. The deposit from the latter gave an excellent *X*-ray powder photograph for α-$Al_2O_3.3H_2O$. It was *not* shaken before analysis of the slightly milky supernatant sol, which was found to contain the proportions of constituents shown in Table I. The sol was specially examined for the presence of basic kations. It was found that 0·15 c.c. of 0·95N-ammonium sulphate just sufficed to cause complete curding of 20 c.c. of the sol. This corresponds to 6·9 mg.-equivs./l. of bound Al$^{\cdots}$, and gives an n value of 35·4 for the micelles. Much quicker filtration of the curd was obtained if 0·3 c.c. of the ammonium sulphate solution was used, the filtrate remaining quite clear and giving no crystals of basic aluminium sulphate after the addition of 12 g. of ammonium sulphate and 7 c.c. of water, even after several days' standing. This shows that the concentration of basic ions must have been very low. The hydrion concentration being taken as still 0·3 mg.-equiv./l., the analytical data correspond to the " free aluminium " being distributed as 2·9 mg.-equivs./l. of $[Al\{Al(OH)_3\}_4]^{\cdots}$ and 83·9 mg.-equivs./l. of $[Al(H_2O)_6]^{\cdots}$. The value of n found after 425 days is fictitiously high owing to inclusion of the stirred-up deposit. It is possible, but not certain, that the analytical composition of the sol was already the same at that age as when 980 days old. The very low basic kation concentration in the 980-days old sol suggests strongly that, in systems of the general composition of sol 9, the basic kations are metastable and tend to deposit their co-ordinated hydroxide upon the microcrystalline hydroxide. It is of interest, in this connection, that the translucent gel obtained as above from this old sol gave an *X*-ray powder photograph with many fairly sharp lines which showed that it consisted essentially of α-$Al_2O_3.3H_2O$ and γ-$Al_2O_3.3H_2O$ (hydrargillite) in about equal proportions. The substance of the micelles in such a sol must be regarded as hydroxide rather than basic salt.

Sols 11 and 12 were peptised with hydrochloric acid, but the hydroxide used for sol 11 had been precipitated in

the cold and that for sol 12 at 100°. Sol 12 was thixotropic but not sol 11. Bound $Al^{\cdots}$ and n could only be calculated for sol 12 for the two dates at which glass-electrode measurements were made owing to the large change in hydrion concentration in this sol with age.

Sol 13 had been prepared from cold-precipitated hydroxide peptised by aluminium chloride. It was the only aluminium hydroxide sol in which no free hydrion (by methyl-red) or aluminium ions could be detected in the filtrates from curds obtained with sodium metaphosphate and potassium ferrocyanide respectively. The sol gave a large proportion of gelatinous deposit on standing, and this was shaken up before analysis. The analysis gave an average n value of 16·5 for the micelles, but a filtration experiment in which three filter fractions and the residue were analysed indicated that the micelles could be subdivided roughly as follows: 10% with n value 8·4; 22% with n value 10·7; 27% with n value 14·6; 41% with n value 26.

Sol 14 was prepared from cold-precipitated hydroxide peptised by the chloride. It was fairly thixotropic and on standing gave a moderate deposit, which was shaken before analysis. The increase in the amount of free aluminium ions in the 25-days old sol is probably due to conversion of some free $Al^{\cdots}$ into basic ions.

Sol 15 was prepared from some of the same hydroxide as was used for sol 14, but it was peptised with hydrochloric acid. This sol was not thixotropic and gave no appreciable deposit on standing: it has been discussed on p. 279. The figures show that the free aluminium ions must have been basic. The figures in parentheses for free aluminium ion are experimental. If 60% of this is supposed to be $[Al(H_2O)_6]^{\cdots}$ and 40% the basic ion $[Al\{Al(OH)_3\}_4]^{\cdots}$, the other figures give the equivalent amount of $Al^{\cdots}$, and these have been used for calculating the data for "bound" $Al^{\cdots}$, un-ionised Al, and n.

sols, prepared respectively from cold- and from hot-precipitated hydroxide. Very probably the thixotropic character is determined by the degree of crystallinity of the particular hydroxide, whether this be α-$Al_2O_3,3H_2O$ or γ-Al_2O_3,H_2O, but the statement sometimes made, that aluminium hydroxide sols prepared by precipitation and subsequent peptisation do not show thixotropy (cf. *Ann. Reports*, 1940, **37**, 117), is clearly incorrect. It is not easy to prepare two samples of aluminium hydroxide with exactly the same physical properties, as may be judged from the data given on p. 288. This is mainly because the extent to which the crystal lattice of either α-$Al_2O_3,3H_2O$ or γ-Al_2O_3,H_2O has been built up depends upon the exact conditions of precipitation, washing, etc., employed. The behaviour of different preparations of hydroxide, and of sols prepared from them, towards acid may vary considerably, as may the thixotropy shown by the sols. Most strong electrolytes, including acids, curd both types of aluminium hydroxide sol. Relatively high concentrations are required in the case of hydrochloric and nitric acids (generally above 0·5N). Clear, transparent sols of very small n value are not curded by these acids. Hydroxide which has been precipitated by means of a large excess of ammonia has a well-developed α-$Al_2O_3,3H_2O$ lattice and is very difficult to dissolve in any but hot concentrated hydrochloric or nitric acid, and this applies to the curds derived from the very milky type of sol. Much the same holds for hot-precipitated hydroxide when this has a well-developed γ-Al_2O_3,H_2O lattice, and for the curds from its sols. Truly amorphous hydroxide dissolves readily even in quite dilute acid.

Dilution has a considerable effect on aluminium hydroxide sols, as illustrated by an experiment with sol 4. This had been prepared from aluminium sulphate, so must have contained some sulphate, but that is immaterial from the present point of view. The total Al content was 1038 mg.-equivs./l. When 8 days old, the sol contained 40 mg.-equivs./l. of free $Al^{\cdots}$; it was then diluted four-fold, and after a further 2 days contained 59·4 ÷ 4 mg.-equivs./l. of free $Al^{\cdots}$. This figure was unaltered 7 days later. The free $Al^{\cdots}$ in the original sol was 48·8 mg.-equivs./l. when it was 20 days old. A ten-fold dilution was then made, and after 10 minutes the free $Al^{\cdots}$ had risen to 55·3 ÷ 10, and after 2 days to 64·7 ÷ 10 mg.-equivs./l. The effect of dilution appears to be rapid.

Preparation of Crystalline Basic Aluminium Sulphates.—(i) *Sol* 16. Aluminium hydroxide, precipitated at 100° from chloride solution with a large excess of concentrated ammonia, was well washed with boiling water. It was mixed as a paste measuring 125 c.c. with a solution of aluminium chloride (3·5 g. of $AlCl_3$ in 21 c.c.) and the mixture was shaken occasionally for several days and then allowed to settle overnight. Much deposit was removed by decantation on the fifth day from the mixing, and a further moderate deposit after another 5 days; no further deposit formed during another 15 days. The translucent sol so prepared was not thixotropic, though the first deposit was. The analysis of this sol was made from 4 to 8 days after the last decantation. The two alternative methods gave the same values for the chlorion concentration. The data again show (cf. sol 15) that the free aluminium must be mainly, or largely, present as basic ions. Convincing proof of this was obtained as follows: 5 C.c. of sol 16 (9 days after last decantation) were curded with 53 c.c. of 0·05N-ammonium sulphate. The filtrate from the curd soon began to deposit small rosettes of minute prismatic crystals, which after 28 hours were filtered off, washed several times with cold water, air-dried, and analysed (Found: Al_2O_3, 40·77; SO_3, 16·48%; $Al_2O_3/SO_3 = 1·94$) (yield 0·05 g.); it did not contain chloride or ammonia, and seemed to be homogeneous under the microscope. Its aluminium content would account for nearly 30% of the total free aluminium in the sol, but the yield of crystalline basic salt was a minimum value, since the bulky curd had not been washed, so as to avoid dilution of the solution from which the basic salt crystallised. In calculating the n value given for sol 16 in Table I, it was assumed that all the "free" aluminium was present as the basic ion $[Al\{Al(OH)_3\}_4]^{\cdots}$ so that only one-fifth of the total "free" aluminium had to be considered as free $Al^{\cdots}$ for the purpose of the calculation.

A week later the rest of the sol (44 c.c.) was worked up similarly, 470 c.c. of the ammonium sulphate

solution being used, but only 0·23 g. of slightly less basic salt was obtained (Found: Al_2O_3, 39·47; SO_3, 16·31%; $Al_2O_3/SO_3 = 1·90$). Sufficient solid ammonium sulphate was now added to the filtrate from the crystals (which had been kept separate from the washings) to double the concentration of this salt. After 8 days' standing a further deposit had separated. This was filtered off, washed with water, air-dried, and analysed (Found: Al_2O_3, 37·00; SO_3, 18·53%; $Al_2O_3/SO_3 = 1·57$) (yield 0·285 g.). Microscopic examination showed that the solid did not consist of the compound crystallising in minute prisms, and it appeared to be amorphous or glassy.

(ii) Two portions of aluminium hydroxide, precipitated by means of ammonia in considerable excess from boiling solutions of 21 g. of the hydrated chloride in 450 c.c. of water, were thoroughly washed with nearly boiling water. The very wet translucent precipitates, each measuring about 150 c.c., were transferred to two 400 c.c. beakers. To one portion were added 5 g. of hexahydrated chloride dissolved in 30 c.c. of water, and to the other, the equivalent (31 c.c.) of 2N-hydrochloric acid. Complete dispersion in the acid seemed to occur at once, but with the aluminium chloride some curd settled out for some time and 3 days were needed for complete dispersion. There was no visible difference in the appearance of the two sols, which were both translucent (but quite opaque), though the sol prepared by means of hydrochloric acid seemed distinctly more thixotropic than the other.

The two sols prepared in this manner were worked up, after a further two days, for the basic salt, a solution of 2 g. of ammonium sulphate in 100 c.c. of water being used for each. The curds were then filtered off, and soon after filtration was started, separation of crystalline basic salt began in the filtrate from the sol which had been peptised by aluminium chloride, but the other filtrate did not give crystals at any time.

The curd from the sol peptised by acid was microscopically free from crystals, whereas the other contained a considerable proportion. The amount lost in this way is unknown and only 0·203 g. of washed, air-dried crystals was obtained, although a further 2 g. of ammonium sulphate in 100 c.c. of water had been added to each filtrate before the crystals were filtered off. Analysis of the filtrate which gave no basic salt, made some time after the second addition of ammonium sulphate, showed it to be 0·138N with respect to aluminium and 0·149N with respect to chlorine. The crystals obtained as above contained Al_2O_3, 40·07; SO_3, 16·89%; $Al_2O_3/SO_3 = 1·85$. The filtrate from the crystals deposited, during 17 days' standing, a further 0·07 g. of amorphous or glassy solid (Al_2O_3, 35·98; SO_3, 19·57%; $Al_2O_3/SO_3 = 1·44$).

The reason for the different behaviour of the two sols prepared in the above experiment has already been discussed and attributed to the persistence of hydrion as such when bound to the micelle of hot-precipitated aluminium hydroxide. The glass-electrode measurement on sol 8 (Table I) also shows that hydrion can survive for a considerable time in sols prepared from this hydroxide.

(iii) Aluminium hydroxide precipitated cold in the amorphous translucent condition is so reactive that after adsorption of hydrion immediate reaction occurs so that a very good yield of basic salt can be obtained from it. The hydroxide was precipitated by the minimum amount of ammonia from a solution of 8 g. of hydrated chloride, filtered off, and washed on a Buchner funnel, the washing not being thorough owing to the slowness of filtration. The hydroxide, 7·5 c.c. of 2N-hydrochloric acid, and water to a total volume of 80 c.c. were well mixed with a spatula. After 3 days all but a little sediment had dissolved to give a faintly opalescent solution. To this were added 2·5 c.c. of an ammonium sulphate solution containing 0·924 g. in 50 c.c., and the mixture filtered. It was hoped that this treatment would remove any trace of residual colloid, though no obvious curding took place.

Another 32 c.c. of the sulphate solution were added with constant stirring to the clear filtrate, whereupon a permanent crystalline precipitate of minute prisms began to form. After 10 mins., during which these increased in amount and size, the rest of the 50 c.c. of ammonium sulphate solution was added. The precipitate was separated after 24 hours' standing, well washed with cold water, and air-dried (yield 3·15 g.) (Found: Al_2O_3, 39·85; SO_3, 14·55%; $Al_2O_3/SO_3 = 2·14$). This exceptionally well-crystallised preparation consisted mainly of (probably) orthorhombic prisms showing straight extinction, but as there seemed to be a trace of amorphous curd present the following treatment was given to remove this.

2·1 G. of the solid were gently stirred for 5 mins. with 50 c.c. of approx. 0·1N-hydrochloric acid, the mixture quickly filtered (pump), and the crystals washed with cold water till free from chloride. After air-drying, the crystals looked sharp and unaltered and there was now no sign of the presence of any amorphous material. As only 1·5 g. of solid were recovered, 0·6 g. had been lost by solution in the acid. The acid filtrate plus washings measured approx. 125 c.c., and after standing for 2 days had deposited crystals, which after washing and air-drying weighed 0·15 g. Microscopic and *X*-ray examination and chemical analysis showed these to be essentially identical with the original preparation and also with the acid-washed crystals (Found: for acid-washed crystals, Al_2O_3, 40·57; SO_3, 15·14%; $Al_2O_3/SO_3 = 2·10$; for crystals separating from acid solution, Al_2O_3, 41·61; SO_3, 15·09%; $Al_2O_3/SO_3 = 2·16$). This remarkable result indicates that the basic salt must have very considerable stability towards acid.

Crystalline basic salt, similar in appearance to that of other preparations, was also made on a small scale by the peptisation of cold-precipitated, translucent aluminium hydroxide with aluminium chloride, but it was not analysed.

Aluminium hydroxide freshly precipitated in the cold is peptised with extreme ease by aluminium chloride, and this is the basis of the modified and simpler procedure used in the following preparations.

(iv) To a solution of 10 g. of aluminium chloride hexahydrate in 75 c.c. of water were added slowly with

constant stirring 22·5 c.c. of approx. 3·2N-ammonia. This gave a perfectly clear sol to which, after 3 days' standing, was added a solution of 2 g. of ammonium sulphate in 30 c.c. of water. The precipitate which separated was mainly an amorphous curd with a proportion of prismatic crystals. After standing for several days, the mixture was diluted to about 150 c.c., and after another 5 days the curd was dissolved by slowly stirring in 2N-hydrochloric acid. After about 7 c.c. of acid had been added, microscopic examination showed that the residual crystals were free from curd. 1·12 G. of washed, air-dried crystals were obtained (Found: Al_2O_3, 39·91; SO_3, 18·91%; $Al_2O_3/SO_3 = 1·64$).

(v) The same quantities were used as in (iv), but directly after addition of the ammonia the mixture was gently boiled for 10 mins. This destroyed the sol, so that on addition of the ammonium sulphate a pure crystalline precipitate was obtained. After two days this was filtered off, washed, and air-dried (Found: Al_2O_3, 39·56; SO_3, 18·64%; $Al_2O_3/SO_3 = 1·67$); yield 2·3 g.

(vi) With a larger proportion of ammonia than was used in the above two experiments it is difficult, if not impossible, to get all the aluminium hydroxide to peptise, but by the following modification this can be done and a nearly theoretical yield of the basic salt obtained. A solution of aluminium chloride, prepared as in (iv), was treated similarly but 32·7 c.c. of ammonia were used, followed by 9 c.c. of 2·05N-hydrochloric acid, and the mixture gently boiled for 20 mins.; all the curd dissolved, and a clear solution was obtained to which, after cooling, were added 2 g. of ammonium sulphate in 30 c.c. of water (Found: Al_2O_3, 40·03; SO_3, 18·77%; $Al_2O_3/SO_3 = 1·67$); yield 4·16 g.

Two other experiments in which minor alterations were made in the general procedure used for the last two preparations gave varying yields of the well-crystallised prismatic crystals, but in both preparations the ratio Al_2O_3/SO_3 was 1·67 [Found: Al_2O_3, (i) 40·11, (ii) 39·75; SO_3, (i) 18·96; (ii) 18·66%]. The *substance* is undoubtedly $5Al_2O_3,3SO_3,17$ or $18H_2O$ (Calc.: Al_2O_3, 40·10, 39·53; SO_3, 18·87, 18·61%, respectively). The hydrate is stable in the air under normal conditions, samples of the various preparations varying in weight by only $\pm$ 0·2% over several weeks. The water is probably to be regarded essentially as "packing" water in the crystals, so the proportion of this would probably depend somewhat upon the size and habit of the crystals in different preparations, since they are small. The crystals are essentially rectangular prisms which extinguish at an angle of about 12° to the length. When the prisms are on edge the extinction appears to be straight.

The well-crystallised, basic salt with $Al_2O_3/SO_3 = 2·16$ consists mainly of rectangular prisms and modifications of these which show straight extinction. The reasons for regarding this as a definite *compound* $13Al_2O_3,6SO_3,76$ or $77H_2O$ are as follows: (1) Its general well crystallised and homogeneous appearance under the microscope: this differs from that of the 1·67 compound, though both are prismatic. (2) It crystallises unchanged from dilute acid. (3) It has a distinctive *X*-ray diagram. (4) The Al_2O_3/SO_3 ratio is practically identical with that (2·17) of the mineral felsőbányite though the degree of hydration differs. The well-crystallised mineral appears to be one of the best-defined basic aluminium sulphate minerals, in spite of the fact that Hintze ("Handbuch der Mineralogie," Vol. 1, p. 4435, 1929–30) casts some doubt upon it. The 76- or the 77-hydrate would require Al_2O_3, 41·77, 41·54; SO_3, 15·12, 15·04%, respectively, whereas the analytical data for felsőbányite correspond to a 61- or a 62-hydrate: Haidinger (*Wien. Sitzungsber.*, 1854, **12**, 188) reported von Hauer as finding: Al_2O_3, 45·63; SO_3, 16·47; H_2O, 37·27%, and regarded the mineral as $2Al_2O_3,SO_3,10H_2O$ (Calc.: Al_2O_3, 44·0; SO_3, 17·2; H_2O, 38·8%).

Filtrates from the basic salt $5Al_2O_3,3SO_3,xH_2O$, on standing for several weeks at room temperature, frequently deposit very characteristic crystals of a third basic salt. The crystals are Maltese-cross twins shaped remarkably like those of the mineral staurolite. They are usually very well developed though rather small. Very often there is only a small re-entrant angle between the two arms of the cross, and the appearance of the crystals then suggests an octahedron at first glance. In other cases the arms of the cross are much more obvious. The two components of the twin extinguish at a few degrees on either side of the diagonal of the Maltese cross. When the crosses are standing on an arm they present a barrel-shaped outline. Very well-formed crystals of the new compound mixed with much amorphous or "glassy" solid had separated from the filtrate of preparation (v) during 15 weeks' standing in a covered beaker, evaporation having reduced the volume of liquid by about one-fifth. The liquid and most of the amorphous solid were decanted, leaving most of the crystals and some amorphous solid adhering to the vessel. Treatment with 50 c.c. of approx. 0·1N-hydrochloric acid dissolved the amorphous curd almost at once, leaving the crystals, which were filtered off (pump), washed with cold water, and air-dried (Found: Al_2O_3, 38·78; SO_3, 17·70%; $Al_2O_3/SO_3 = 1·72$); yield 0·239 g. Even 2N-hydrochloric acid only attacked the crystals very slowly in the cold, though they dissolved rapidly on heating.

(vii) 16·9 C.c. of approx. 3·2N-ammonia were added with constant stirring to a solution of aluminium chloride as in (iv). The clear solution was boiled for 15 mins., diluted to approx. 400 c.c., and 1·5 g. of ammonium sulphate in 25 c.c. of water were added to the warm solution. No precipitate had separated after 12 hours, so a further 1 g. of sulphate was added. A relatively small, bulky precipitate (apparently amorphous or glassy) had separated after 2 days and was removed by filtration. After standing for 19 weeks in a covered beaker, the filtrate deposited a considerable amount of solid. This consisted in part of the coarse Maltese-cross twins and in part of much finer material which showed no definite structure under the microscope and may have been "glassy solid." The mixture was well stirred, and the bulk of liquid (now about 300 c.c.) decanted together with most of the fine solid; the latter was filtered off (pump), washed

with water, and air-dried (0·25 g.). To the 50 c.c. of mixture which contained the coarse crystals were added 5 c.c. of 2N-hydrochloric acid which dissolved the fine material rapidly. After a few minutes the coarse crystals were similarly filtered off, washed, and dried (0·68 g.).

The fine crystals, slightly contaminated with the coarse, had $Al_2O_3/SO_3 = 1·64$ (Found: Al_2O_3, 35·72; SO_3, 17·06%), and the latter had $Al_2O_3/SO_3 = 1·72$ (Found: Al_2O_3, 39·16; SO_3, 17·85%). The *hydrate* $12Al_2O_3,7SO_3,75$ or $76H_2O$, for which $Al_2O_3/SO_3 = 1·714$, requires Al_2O_3, 39·06, 38·84; SO_3, 17·87, 17·77%, respectively.

The following experiment shows that a relatively large proportion of ordinary aluminium ions can coexist in solution with very basic ions. The procedure was as in experiment (vi) except that 20 c.c. of 2·05N-hydrochloric acid were added and the mixture was boiled till clear, 2·75 g. of ammonium sulphate in 10 c.c. of water being added to the hot solution; yield of washed, air-dried solid 2·7 g. (Found: Al_2O_3, 35·90; SO_3, 17·79%; $Al_2O_3/SO_3 = 1·58$). 10 G. of ammonium sulphate were added to the filtrate (without washings), and after standing for a week a considerable separation of well-formed square and octahedral crystals had occurred. These were separated by settling and decantation from much fine amorphous solid which had also formed. 0·6 G. of washed, air-dried crystals was obtained and another 0·1 g. after a further 3 months' standing, but much was lost during decantation and washing. Probably about 2·5 g. of these crystals in all had been formed. They gave a strong reaction for ammonia, were isotropic, and consisted of ammonium alum contaminated with a little of the insoluble basic material (Found: Al_2O_3, 11·62; SO_3, 35·44. Calc.: Al_2O_3, 11·26; SO_3, 35·32%).

An *X*-ray rotation photograph about the cube axis of one of the crystals proved conclusively that these did in fact consist of ammonium alum, for the atomic spacings calculated from the photograph agreed with those given for this alum by Lipson and Beevers (*Proc. Roy. Soc.*, 1935, *A*, **148**, 666).

Under certain conditions an ammonium basic aluminium double sulphate separates as small very brilliant crystals from the filtrates of sols treated with ammonium sulphate. Under the microscope these resemble regular octahedra, but they are strongly double refracting. They are single crystals and not twins, though there is a slight superficial resemblance to the maltese-cross twins formed by the basic sulphate $12Al_2O_3,7SO_3,75$ or $76H_2O$.

(viii) To 10 g. of hydrated aluminium chloride in 80 c.c. of water were added fairly quickly 32·7 c.c. of approx. 3·2N-ammonia, which gave a faintly alkaline mixture. This was then poured into about 80 c.c. of boiling water, and the whole boiled for 10 mins. A translucent suspension was obtained which was set aside over the week-end. A bulky gel had settled out, with a moderate amount of clear liquid above it. The filtrate from the gel was treated with a solution of 1 g. of ammonium sulphate in 10 c.c. of water. This caused separation of a small amount of non-crystalline curd, which was filtered off to give an absolutely clear filtrate. To this were added 10 g. of solid ammonium sulphate, which dissolved without producing any further precipitate. After 16 days' standing a small deposit of crystals with the above-described characteristics was filtered off. Unfortunately, the crystals were washed with water, which caused decomposition and rendered them opaque—the partly decomposed crystals weighed 0·055 g. The volume of solution from which they had separated was approx. 125 c.c. The filtrate from these (without washings), after 6 weeks' standing, had given a further small deposit of the crystals, which was filtered off, washed (without decomposition) with 3 c.c. of 50% alcohol, and air-dried. The crystals were quite unaltered in appearance by this treatment; yield 0·037 g. (Found: NH_3, 4·2; Al_2O_3, 31·3; SO_3, 24·8. $[NH_4]_4[Al\{Al(OH)_3\}_4]_3[SO_4]_5[H_2O]_{32}$ requires NH_3, 4·2; Al_2O_3, 31·4; SO_3, 24·6%). As the ammonia estimation had to be made colorimetrically with Nessler reagent, it is probably subject to an uncertainty of $\pm$ 10%.

The conditions needed for the separation of this double *salt* appear to be a low concentration of the basic ion and a relatively very high concentration of ammonium and sulphate ions.

Chromium Hydroxide Sols.

Chromium chloride and hydrochloric acid are equally effective as peptising agents for chromium hydroxide: the sols produced are identical which ever agent is employed, and they are very stable. We have found no indications of any liberation of bound kation due to either age or dilution. Chromium hydroxide sols gave no precipitate with hydrochloric acid in any circumstances. Table II gives some of the results obtained with these sols. All those listed were peptised by means of chromium chloride, except No. 7 for which hydrochloric acid was used. The most striking feature of the table is the marked tendency for the sols to have an n value close to 4. This appears to show that the micelles are adsorptively saturated and that this condition can be attained with little if any excess of peptising agent. It may be concluded that the charge on the micelles is due, almost entirely, to adsorbed chromium ions, since the sols have such a very small acidity.

Differences found in the free chromium-ion content of several of the sols at different ages are attributed to uncertainties in the analytical methods. High results for free chromium when little or none is present are due to the use of slightly too little ferrocyanide for precipitation of the micelles.

All the hydrion figures given in the table were obtained by the titration method after curding with metaphosphate. They are probably too high, since metaphosphate causes hydrolysis of chromium chloride (see p. 279), and their chief value is in showing that the hydrion concentration of those sols is very low.

Only one glass-electrode measurement was made on a chromium sol, *viz.*, on a 5-fold dilution of sol 3 when this was 1470 days old. Analysis of the diluted sol gave:

Total Cr.	Un-ionised Cr.	Bound $Cr^{\cdots}$.	Free $Cr^{\cdots}$.	$H^{\cdot}$ (by glass electrode).	Cl'.	n.
1728	1299	319	111	1·16	431	4·07
whence the undiluted sol contained						
8640	6495	1595	555	5·8	2155	—

It is seen that 5-fold dilution caused no separation of previously bound kations. The diluted sol underwent no further appreciable change on ageing.

TABLE II.

Sol.	Total Cr.	Un-ionised Cr.	Bound $Cr^{\cdots}$.	Free $Cr^{\cdots}$.	$H^{\cdot}$.	Cl'.	n.	Age (days).
1	1580	1184	232	164	3	399	5·1	3
2	1944	1595	350	0	0	351	4·6	3
3	8640	6483	1636	521	3·8	2163	3·96	38
	,,	6476	1609	555	6	2170	4·03	83
	,,	6482	1618	540	(38)	2164	4·01	379
	,,	6502	1618	520	(77)	2144	4·02	510
	,,	(6523 ?)	(1562 ?)	(627) (555 ?)	7·6	2123	4·17	1270
4	4372	3538	818	16	3	837	4·33	7
	4435	3600	835	0	0·9	836	4·31	18
	4432	3502	830	0	1·5	832	4·22	52
	4555	3693	852	10	0·9	863	4·34	322
6	6786	5442	1318	26	0	1344	4·13	7
	,,	,,	1338	6	0	,,	4·07	56
	,,	,,	1319	26	0	,,	4·13	165
7	3294	2594	625	75	8	708	4·15	3
	,,	2587	623	74	0·8	,,	4·15	161
	3255	2542	603	110·5	0·9	714	4·21	323

Sol 3 became somewhat more concentrated with increasing age owing to slight evaporation. The figures given in the table were obtained from the experimental figures by recalculation to a constant average figure for total chromium. The hydrion figures 38 and 77 for this sol are clearly much too high. A constant value of 6 for the hydrion concentration, based on the glass-electrode measurement on the diluted sol, has been assumed in calculating the bound $Cr^{\cdots}$. The value 627 for free $Cr^{\cdots}$ at age 1270 days must be wrong. A value 555 derived from the diluted sol analysis has been used to calculate the bound $Cr^{\cdots}$. The chlorion concentration at age 1270 days was also determined by direct precipitation with silver nitrate of a nitric acid digestion of the sol. The value 2113 so obtained does not support the view that the low value 2123 obtained by the usual method was due to some chlorion having become "masked" in the old sol.

Sols 3 and 4 showed strikingly different behaviour in two respects which can be attributed to the great difference in the amount of free chromium ion in the two sols. Sol 4 was much more viscous than sol 3, though the latter was nearly twice as concentrated. The viscosities were measured in an Ostwald viscometer at 16° with the following results:

	Specific gravity (S).	Time readings (N), secs.	$S \times N$.	Relative viscosity, SN/S_wN_w.
Water	1·000	62	62	1
Sol 3	1·257	344	432·4	6·97
Sol 4	1·129	524	591·6	9·54

The lower viscosity of sol 3 appears to be due to the presence of free chromium chloride, which was 6·4% of the total chromium. Sol 3 retained its highly mobile character for 3½ years with no deposit. Sol 6 was also much more viscous than sol 3 though less concentrated. It is well known that when a sol approaches "purity" by means of dialysis its viscosity increases often up to a point at which spontaneous coagulation occurs. On evaporation over sulphuric acid at room temperature, sol 3 gave a glassy residue which dissolved in cold water on standing for several hours.* Analysis of the regenerated sol so obtained gave:

Total Cr.	Un-ionised Cr.	Bound $Cr^{\cdots}$.	Free $Cr^{\cdots}$.	$H^{\cdot}$.	Cl'.	n.
609·5	457·9	151·6	0	1·7	153·3	3·02

showing that the whole of the chromium ions which were free in sol 3 had become bound, with corresponding reduction in the n value. If the hydrion (determined by the titration method) is taken to be zero, the n value becomes 2·98. The high concentration of chromium ions produced by the evaporation may have caused some less basic kation to be formed than is present in the micelles which have an n value of 4.

When sol 4 was similarly evaporated, the glassy residue was only very slowly dissolved by cold water, about 3% having dissolved after 24 hours, but all dissolved slowly in warm water. This sluggishness may be due simply to greater initial dehydration and consequent slower rehydration and dispersion. Very insoluble green products with a conchoidal glassy fracture are often obtained as deposits during the preparation of

* Some of the glassy residue which had been kept for 3 years took 3 days to disperse completely in cold water.

chromium hydroxide sols, but only if the proportions of hydroxide and of chromium chloride or hydrochloric acid employed are such as would represent a ratio $Cr(OH)_3 : CrCl_3$ of more than 4. Several such deposits obtained during the preparation of sols 4 and 6 had compositions between about $[Cr(OH)_3,xH_2O]_{5\cdot86}CrCl_3$ and $[Cr(OH)_3,xH_2O]_{6\cdot33}CrCl_3$, where the value of x depended upon the precise conditions of drying but was about 3 for "air-drying" at room temperature. The deposits obtained during the preparation of sol 7, where hydrochloric acid was the peptising agent and in which successive amounts of the hydroxide were added to the acid, had smaller n values, however. These ranged between 4·43 for the earlier deposits and 6·04 for the last deposit. The sols finally produced contained little if any free chromium ions, as can be seen from the tables, and their micelles had an n value of about 4. The nature of these glassy products has been discussed on p. 281.

Ferric Hydroxide Sols.

We have prepared and examined two different types of ferric hydroxide sol: (*a*) those prepared by peptisation of cold-precipitated ferric hydroxide with either ferric chloride or hydrochloric acid, and (*b*) those obtained by addition of boiling water to ferric chloride.

It is not generally realised how difficult it is to obtain pure iron compounds. Most of those usually found in laboratories, even when of "AnalaR" quality, contain more or less manganese, and the commercial ferric chloride is often very impure: zinc as well as manganese may be present in considerable amount. Ferric hydroxide sols prepared from such materials contain most of the zinc or manganese as free kations. A sample of Kahlbaum's ferrous ammonium sulphate, stated to be free from manganese, was actually free from both manganese and zinc but contained a large amount of aluminium. This was about 2·5 equivs. % of the total (Fe + Al) and was present as crystals of ammonium alum (identified by refractive index and other optical properties). Some of our sols were prepared from this material, which was purified by precipitation, hot, with excess of sodium hydroxide after oxidation with nitric acid. After washing, digestion with more hydroxide, and further washing, the precipitate was dissolved in the minimum amount of concentrated hydrochloric acid, and the diluted solution precipitated cold with excess of ammonia. Most of our sols were, however, prepared from "AnalaR" anhydrous ferric chloride, which was found to be the purest purchasable iron compound, containing only 0·07 part by weight of manganese per 100 parts of iron. The statements on the labels of this material that "sodium and other metals" amount to 0·04% is misleading, since any manganese present would be carried down by the iron and missed by the method of analysis used for label purposes.

TABLE III.

Sol 20 (n = 0·5 or 1·5). Prepared by addition of 500 c.c. of boiling water to 3 c.c. of approximately 30% ferric chloride solution (Found: Total Fe, 43·9; total Cl, 43·7 mg.-equivs./l.).

Ageing shown by the increase of total free iron in solution:

Age, days	1	3	21	31	55	73
Free iron, mg.-equivs./l.	16·3	18·8	23·8	25·4	25·2	24·7

Free $H^{\cdot}$ by the glass electrode was 5·9 mg.-equivs./l. when 55 days old. Sols 28, 29, and 30 were prepared in a similar manner.

Sol 28; n = 6·1 or 7·1; total Fe = 83.

Total free $Fe^{\cdot\cdot\cdot}$.	Free $H^{\cdot}$.	Cl'.	Age (days).	Total free $Fe^{\cdot\cdot\cdot}$.	Free $H^{\cdot}$.	Cl'.	Age (days).
42·8	—	83	3	—	23·6	83	9
—	22·9	"	4	50·8	—	"	11
47·8	—	"	5	53·8	25·1	"	33
50·4	—	"	7				

Sol 29; n = 1·3 or 2·3 (at 21 days); total Fe = 117·4.

53·1	—	117·1	2 (hours)	70·9	24·0	117·1	10
56·6	—	"	1	72·4	28·8	"	12
61·0	—	"	2	73·5	—	"	15
63·2	—	"	3	74·9	28·2	"	17
66·3	38·0	"	5	76·6	22·9	"	21
68·4	31·6	"	7	87·3	—	"	276

Sol 30; n = 6·2 or 7·2; total Fe = 136·8.

72·9	—	135·7	2 (hours)	88·9	30·9	135·7	10
76·3	—	"	1	90·8	30·9	"	12
82·1	31·6	"	2	103·5	—	"	119
84·4	30·9	"	4	103·5	27·6	"	220
88·2	33·9	"	7				

Sols prepared by the action of boiling water upon ferric chloride contain relatively more free hydrion than do those prepared by peptisation of ferric hydroxide. They also age more rapidly by some process which leaves the concentration of free hydrion practically constant while the amount of free ionic iron increases. The red sols become more orange with age. It is suggested that initially these sols contain micelles of (FeO·OH) carrying adsorbed hydrion. On standing at room temperature, the bound hydrions slowly react with the micelles to set free ordinary ferric ions. If one assumes that no bound hydrions were left but only bound $Fe^{\cdot\cdot\cdot}$ when the last readings on each sol were made, the smaller n values shown against the sol numbers can be calculated for the dates of the last readings. The presence of basic ions in the intermicellar

liquid would lower the n values still further. If, however, it is supposed that all the bound kations were hydrions, then the larger values of n may be calculated for the dates of the last readings. We consider that the higher n values are the more probable, and that in this type of sol, the charge on the micelles is due mainly to bound hydrion. The change which occurs on ageing is, of course, a sort of reversal of the original hydrolysis by which the sol was formed. This reversible process is less simple than is represented by such equations as (i) $Fe^{\cdots} + HOH \rightleftharpoons [FeOH]^{\cdot\cdot} + H^{\cdot}$ or (ii) $Fe^{\cdots} + 3HOH \rightleftharpoons Fe(OH)_3 + 3H^{\cdot}$, and is more in keeping with the complex equation (iii) $nFe^{\cdots} + 3nHOH \rightleftharpoons [Fe(OH)_3]_nH^{\cdot}_{3n}$. It would seem that the actual reversible hydrolysis involves reactions similar to (i) and (ii) but occurring between the bound kations and the hydroxide substrate of the micelles.

The hydrion concentrations were all obtained by means of the glass electrode. The variations for any one sol are probably within the limits of error of the measurements.

Table III gives our results with some of these hydrolysis sols.

The results shown in Table IV for sols prepared by the cold method suggest that the micelles would be approximately saturated with bound kations at an n value of about 7. The values for free hydrion which are enclosed in parentheses in Table IV were obtained by the metaphosphate method and are therefore probably too high. They are given because they serve to show that there is almost certainly a slow but definite increase in the acidity of these sols on ageing.

An unsuccessful attempt was made to peptise, by means of hydrochloric acid, ferric hydroxide which had been precipitated at about 100° and washed with ammonia and water at this temperature. The mixture on the first day was found to contain total Fe, 1341; total Cl, 340 mg.-equivs./l., the chlorine being determined after solution of the mixture in nitric acid. Even after 39 days with frequent shakings, the mixture gave a

TABLE IV.

Bound $Fe^{\cdots}$.	Free $Fe^{\cdots}$.	Free $H^{\cdot}$.	Cl′.	n.	Age (days).	Bound $Fe^{\cdots}$.	Free $Fe^{\cdots}$.	Free $H^{\cdot}$.	Cl′.	n.	Age (days).
Sol no. 19, peptised by 2N-HCl; total Fe = 1886; un-ionised Fe = 1689.											
170	27	(5·5)	210	9·9	8	168·8	28·2	(6·5)	—	10·0	150
184	13	(2·5)	—	9·2	11	150	47	(9·5)	—	11·2	241
179	18	(3·5)	—	9·4	14	137	60	(18·0)	—	12·3	610
167	30	(4·5)	—	10·1	84	125	72	—	211·3	13·5	1134
						—	—	12·9	—	—	1176
Sol no. 22, peptised by 2N-HCl; total Fe = 2554; un-ionised Fe = 1988.											
255	311	—	584	7·8	1	230	336	—	584	8·6	24
257	309	—	,,	7·7	3	225	341	19·1	,,	8·8	46
264	302	—	,,	7·5	5	213	353	—	,,	9·3	71
255	311	—	,,	7·8	7	196	369	17·0	,,	10·1	115
221	345	—	,,	9·0	14	180 *	378	—	576	10·3	492
Sol no. 23, peptised by $FeCl_3$; † total Fe = 2819; un-ionised Fe = 2173.											
273	373	—	666	8·0	1	266	380	—	666	8·2	24
274	372	—	,,	7·9	3	242	404	24	,,	9·0	46
294	352	—	,,	7·4	7	241	405	—	,,	9·0	72
277	369	—	,,	7·8	9	—	—	15·5	,,	—	116
279	367	—	,,	7·8	14						
Sol no. 24, peptised by $FeCl_3$; ‡ total Fe = 2348; un-ionised Fe = 1893.											
221	235	—	470	8·6	2	187	269	—	470	10·1	20
216	240	—	,,	8·8	5	174	282	13·8	,,	10·9	29
200	256	—	,,	9·5	12	187	269	—	,,	10·1	62
194	262	—	,,	9·8	15	—	—	14·5	—	—	98
Sol no. 24a, peptised by $FeCl_3$; § total Fe = 2333; un-ionised Fe = 1890.											
165	278	—	472	11·5	3	138	305	—	472	13·7	16
151	292	—	,,	12·5	6	140	303	29	,,	13·5	30
147	296	—	,,	12·9	9	123	320	—	,,	15·4	63
141	302	—	,,	13·4	12	126	317	—	,,	15·0	96

* A heavy sediment had settled out from this sol after 490 days and, though vigorously shaken, some remained adhering to the flask when a portion of the sol was removed for analysis, so it then had total Fe = 2407, un-ionised Fe = 1849. The yellow sediment was shown to retain 19% of its total chlorine content after digestion with hot ammonia. In calculating the n values of sols 19 and 22 a steady value of 13 and 18 respectively has been taken for the hydrion concentration. The bound kation has been assumed to be only $Fe^{\cdots}$.

† Free $H^{\cdot}$ taken as 20 throughout in calculating n values for this sol.

‡ Free $H^{\cdot}$ taken as 14 throughout in calculating n values for this sol.

§ After sol 24 had been prepared half of it was heated to 85° and then kept at about 60° for 14 hours. This sol (24a) was very opaque. Heating has increased the free hydrion and free iron. Although this is somewhat similar to the effect of age, there is a difference, for in sol 24 little if any of the chlorine was masked even after 62 days, whereas sol 24a after 3 days gave 472 mg.-equivs./l. of chlorine by the method in which the sol was first destroyed by nitric acid, while precipitation of the sol by ammonia and thorough washing of the curd by ammonia only gave in the filtrate chlorine equivalent to 419 mg.-equivs./l. in the sol. When the sol was 96 days old a value of 441 mg.-equivs./l. of chlorine was found by the direct ammonia method.

TABLE IV (*contd.*).

Bound $Fe^{...}$.	Free $Fe^{...}$.	Free $H^{.}$.	Cl'.	n.	Age (days).	Bound $Fe^{...}$.	Free $Fe^{...}$.	Free $H^{.}$.	Cl'.	n.	Age (days).
Sol no. 25, peptised by $FeCl_3$; ‖ total Fe = 2740; un-ionised Fe = 2452.											
260	28	—	299	9·4	1 (hr.)	263	25	—	299	9·3	13
267	21	—	,,	9·2	1	261	27	—	,,	9·4	21
274	14	(1·6)	,,	8·9	2	237	51	11	,,	10·3	58
276	12	(3·8)	,,	8·9	5	210	78	—	,,	11·7	229
271	17	—	,,	9·0	7						
Sol no. 26, peptised by slow addition of $Fe(OH)_3$ to 0·2N-HCl; ¶ total Fe = 487; un-ionised Fe = 441.											
35	11	(0·8)	57	12·6	4	35	11	10·6	57	12·6	71
35	11	(6·2)	,,	12·6	11	33	13	(11·6)	,,	12·4	118
36	10	(6·6)	,,	12·3	19	33	13	8·9	,,	12·4	125
33	13	(7·0)	,,	12·4	35	30	16	(11·9)	,,	14·7	243
Sol no. 27, prepared by adding $Fe(OH)_3$ to 0·2N-HCl; total Fe = 510; un-ionised Fe = 455·7.											
43	11·3	(8·5)	61·4	10·6	5	41	13·3	—	61·4	11·1	60
43·5	10·8	—	,,	10·5	7	38·3	16·0	—	,,	11·9	130
42	12·3	7·1	,,	10·9	11	24·6 **	24·4	(12·4)	,,	18·7	265

Sol 31 *and its dilutions.* No glass-electrode measurements were made on this sol, but results with other sols indicate that the hydrion concentration of sol 31, prepared by peptisation of $Fe(OH)_3$ with 2N-HCl, would have been about 11 mg.-equivs./l. This value has been assumed in calculating the n value of this sol.

Total Fe = 2468; un-ionised Fe = 2184.

Bound $Fe^{...}$.	Free $Fe^{...}$.	Cl'.	n.	Age (days).	Bound $Fe^{...}$.	Free $Fe^{...}$.	Cl'.	n.	Age (days).
226·2	57·8	295	9·7	3	224·4	59·6	295	9·7	17
232·7	51·3	,,	9·3	5	219·4	64·6	,,	10·0	21
225·6	58·4	,,	9·7	13					

5-Fold dilution.			10-Fold dilution, when sol 31 was 13 days old.		20-Fold dilution, when sol 31 was 13 days old.	
Age of sol 31 at dilution, days.	Time since dilution, days.	Free $Fe^{...}$.	Time since dilution, days.	Free $Fe^{...}$.	Time since dilution, days.	Free $Fe^{...}$.
13	3	60	1	51·2	1	35
13	5	66·5	3	58·4	3	41·7
17	1	64	5	55·7	6	45·3
19	1	64·9				

Actual results for free $Fe^{...}$ have been multiplied by 5, 10, and 20, respectively, so as to make the effect of dilution clearer. The results, taken in conjunction with that of the single dilution of sol 26, suggest that the effect of dilution is to upset the hydrolytic equilibria with replacement of a certain amount of the free $[Fe(H_2O)_6]^{...}$ ions by the equivalent amount of hydrion, the hydroxide so produced presumably becoming attached to the micelles. This would indicate that there are practically no free basic kations in these ferric hydroxide sols, but only ordinary ferric ions and hydrions.

‖ About 2% of the chlorine was held up by the curd obtained with ammonia at age 58 days. Hydrion concentration taken as 11 throughout in calculating n.

¶ Sol 26 gave a slight deposit on standing until about 40 days old, when peptisation seemed complete. Hydrion concentration taken as 11 in calculating n. Ageing of this sol appears to be very slow. The curd obtained with ammonia when it was 4 days old held up no chlorine, whereas that at 118 days held up about 1% of the total. A 10-fold dilution of sol 26 was made when it was 125 days old, and after 2 days the dilution contained 4·3÷10 mg.-equivs./l. of $Fe^{...}$ and 16·6÷10 mg.-equivs./l. of $H^{.}$.

** In this solution, un-ionised Fe = 461.

large deposit on standing and contained 270 mg.-equivs./l. of free $Fe^{...}$; 7·4% of the total chlorine was held up by the curd obtained by addition of ammonia after repeated washing with ammonia.

Lanthanum Hydroxide Sols.

Lanthanum hydroxide is such a strong base that it is extremely difficult to prepare its sols quite free from carbonate. This was not fully realised until much work on these sols had been done. Apart from this difficulty, they are among the easiest hydroxide sols to prepare, and in fact, auto-peptisation occurs so readily on washing the hydroxide that this is not easily obtained pure; in order to prevent this, a sufficient concentration of hydroxyl ions must be maintained in washing out the chloride. Addition of ammonia does not always suffice for this purpose, and some pure sodium hydroxide should be added in such cases; washing can be completed with pure water.

The oxalate, $La_2(C_2O_4)_3.10H_2O$, was ignited in platinum, and a neutral solution of the chloride prepared by dissolving the lanthana in the calculated amount of hydrochloric acid. This solution was used for preparing lanthanum hydroxide, and also for peptising it in sols 7 and 8, hydrochloric acid being used for this purpose for all the other sols given in Table V. When protected from carbon dioxide, lanthanum hydroxide sols are very stable and the bound lanthanum ions then only become free very slowly. Treatment

of the sols with carbon dioxide liberates lanthanum ions rapidly and causes a gel to separate. This is not the normal effect of a coagulating anion for this does not displace the bound kations. Carbonic acid, even in very low concentration, probably acts on these sols as follows: (*a*) on account of the strongly basic character of lanthanum hydroxide, bound lanthanum kations are displaced by the equivalent amount of hydrion with relative ease; (*b*) the bound hydrion then reacts with the substrate to produce more lanthanum ions which probably remain bound unless displaced by more hydrion; (*c*) carbonate ions exert the well-known effect of bivalent anions and ultimately cause curding of the sol; (*d*) continued action of carbonic acid will cause complete carbonation of the original hydroxide.

The ageing of lanthanum hydroxide sols is shown in Table V. Sols 7 and 8 were preserved in stoppered bottles in a desiccator containing soda–lime, and sol 3 was kept in a stoppered bottle, but not in a desiccator. Sols 9 and 10 were kept in flasks, closed by tightly fitting rubber bungs, but not in a desiccator.

There had been some contact with the atmosphere during the preparation of these sols; it was probably least with sols 9, 11, and 13, but nevertheless, treatment of sol 9 with acid showed the presence of traces of carbonate. The experiment with sol 10 shows the marked effect of carbon dioxide deliberately introduced into the system. It is relatively easy to protect the sols from this gas once they are prepared. The chief difficulty arises in the preparation of the hydroxide, especially in its collection and washing.

The following conclusions follow from our experiments. (i) Peptisation by either hydrochloric acid or lanthanum chloride is complete after 3 days or less. (ii) The sols age extremely slowly when protected from carbon dioxide (sols 7 and 8) but more rapidly when slow access of this gas can occur (sol 9). (iii) The sols are completely precipitated, with formation of crystalline lanthanum carbonate, when deliberately treated with carbon dioxide (sol 10). (iv) Dilution with conductivity water has a negligible ageing effect in liberating lanthanum ions (sol 10); ordinary distilled water has a marked effect on account of the carbon dioxide present (sol 3a). (v) Sols with an average n value at least as low as 7·1 can be prepared, although in most cases the value was much greater than this.

TABLE V.

Lanthanum Hydroxide Sols.

Sol. No.	Total La.	Un-ionised La.	Bound $La^{\cdots}$.	Free $La^{\cdots}$.	Cl'.	n.	Age (days).
3	1778	1539	88	151	239	17·5	9
	,,	,,	87	152	,,	17·7	14
	,,	,,	,,	,,	,,	,,	25
	,,	,,	80	159	,,	19·2	163
3a	1844	1606	84	156	240	19·1	17
dilution 10	with	Free $La^{\cdots}$	73 ÷ 10	167 ÷ 10	—	—	—
dilution 20	ordinary	within one	66 ÷ 20	173 ÷ 20	—	—	—
dilution 40	distilled	day after	58 ÷ 40	181 ÷ 40	—	—	—
dilution 50	water	dilution	47 ÷ 50	192 ÷ 50	—	—	—
7	468	431·8	20·2	16·0	36·2	21·4	3
	,,	,,	20·9	15·3	,,	20·7	9
	,,	,,	17·4	18·8	,,	24·8	119
	,,	,,	17·9	18·3	,,	23·9	561 *
8	1352	1063	33	256	289	32·2	1
	,,	,,	57	232	,,	18·6	2
	,,	,,	65	224	,,	16·3	3
	,,	,,	60	229	,,	17·7	5
	,,	,,	58	233	291	18·2	116
9	1064	904·9	105·1	54	159·1	8·6	3
	,,	,,	104·6	54·5	,,	8·7	4
	,,	,,	103·9	55·2	,,	,,	5
	,,	,,	97·3	61·8	,,	9·3	7
	,,	,,	87·3	71·8	,,	10·4	35
	,,	904·6	79·7	79·7	159·4	11·3	143
10	1007	848·5	54·1	104·4	158·5	15·7	3
	,,	,,	,,	,,	,,	,,	12
	,,	,,	47·9	110·6	,,	17·7	81
dilution 50	with conductivity water when sol 10 was 12 days old: two separate experiments one day after dilution		46·3 ÷ 50 55·6 ÷ 50	112·2 ÷ 50 102·9 ÷ 50	— —	18·3 15·3	— —
11	142·4	124	6·4	12·0	18·4	19·4	3
	,,	,,	6·2	12·2	,,	20	8
	,,	,,	5·9	12·5	,,	21·0	16
13	72·6	44·3	6·2	22·1	28·3	7·1	1
	,,	,,	,,	,,	,,	,,	13

* Evaporation in sodium hydroxide desiccator between 119 and 561 days had raised the concentration of total La to 593. Experimental figures have been reduced in the ratio 468/593.

Table V shows that the n values of the sols are usually large even when a high concentration of lanthanum ions is present, but there is no simple relationship between the value of n and the concentration of lanthanum ions. This suggests that some factor other than a simple adsorption of lanthanum ions is involved. We

consider that the large n values are due to partial carbonation of the micelles. If this is correct, it follows that the lanthanum (and neodymium) hydroxide sols are not strictly comparable with the other hydroxide sols dealt with in this paper. They are sols in which the micellar charge has been partly neutralised by addition of carbonate ions. It is probable, from the amount of free lanthanum or neodymium ions present, that the micelles of all the sols were adsorptively saturated.

A few of the lanthanum sols (*e.g.*, No. 13) were translucent, but most had a milky appearance and had a marked tendency to form deposits on standing for even a short time. They behaved, in fact, more like suspensions of charged particles than true sols. For instance, by filtering sols 9 and 10 through a Whatman No. 50 (hardened) paper on the pump, a gel and a clear solution of lanthanum chloride were obtained.

The data in the table refer to sols which had been shaken up immediately before removal of samples for analysis. The tendency of many of the lanthanum sols to give deposits on standing and their lack of homogeneity can be illustrated by the behaviour of sols 9 and 11. The remainder of sol 9, after the data recorded in Table V had been obtained, was kept without shaking, and the translucent liquid above the deposit was analysed when the sol was 163 and 453 days old. The results obtained were:

Total La.	Un-ionised La.	Bound $La^{\cdots}$.	Free $La^{\cdots}$.	Cl'.	n.	Age (days).
595·3	440·6	70·4	84·3	154·7	6·3	163
173·4	41·6	27·4	104·4	131·8	1·5	453

It is evident that only micelles with very small n values were left in the 453-days old sol. The sol still gave a white precipitate (which soon dissolved) on addition of 2N-nitric acid, which suggests that the micelles were still large in spite of the small n value.

100 C.c. of sol 11 when 8 days old were allowed to settle in a tightly corked, graduated cylinder, and the upper 95 c.c. separated from the lower 5 c.c.; the deposit in the latter was washed twice by decantation and both this and the upper sol were analysed. The results for the latter after 4 days' settling were:

Total La.	Un-ionised La.	Bound $La^{\cdots}$.	Free $La^{\cdots}$.	Cl'.	n.
121·9	104·4	5·7	12·2	17·9	18·2

and the washed deposit corresponded closely to $[La(OH)_3]_{50}LaCl_3,xH_2O$. The total La_2O_3 in the deposit from the original 100 c.c. was about one-tenth of that in the settled sol, so the n value of the original sol agrees closely with that calculated from the values for settled sol and deposit.

Addition of more hydrochloric acid to the sols with high n values has little effect on this value, but there is an increase in the amount of free $La^{\cdots}$ which is roughly equivalent to the added acid. This agrees best with the view that the micelles are adsorptively saturated but partly carbonated. In spite of the tendency of these sols to become carbonated, a very small crystalline deposit from a sol which was 130 days old may have been lanthanum hydroxide. After being washed and dried at about 35°, its loss on ignition was 15·1% [Calc. for $La(OH)_3$: $1\frac{1}{2}H_2O$, 14·2%]. It contained a trace of chloride but was free from carbonate. It consisted of small spherulitic nodules and also many square to barrel-shaped crystals. Some of these showed straight extinction, others oblique. The crystals were probably either orthorhombic or monoclinic. The birefringence was low with two indices about 1·71 and 1·73 in the case of the larger crystals and the spherulites had a mean refractive index of about 1·72. The crystals were too small for detailed examination. These values and the general behaviour are not inconsistent with the crystals' being crystallographically similar to the monoclinic gibbsite, γ-$Al(OH)_3$, which has refractive indices, α 1·566 and γ 1·587, but they may have consisted of basic chloride. The index of the orthorhombic plates of $La_2(CO_3)_3,8H_2O$ is considerably lower than 1·7, β being 1·58 and γ 1·60.

Sol. No. 13 was much more translucent than a 5-fold dilution of sol No. 11.

Treatment of sol no. 10 with carbon dioxide. 90 C.c. of sol No. 10 when 3 days old were placed in a 250-c.c. flask. The air in this was displaced by carbon dioxide which was not bubbled through the sol. The next day a sample was withdrawn for analysis, and more carbon dioxide passed into the flask. This treatment was repeated at intervals of two days.

Total La = 1007; un-ionised La = 848·5.

Bound $La^{\cdots}$.	Free $La^{\cdots}$.	Cl'.	n.	Age of sol (days).	Time of action of CO_2 (days).	Bound $La^{\cdots}$.	Free $La^{\cdots}$.	Cl'.	n.	Age of sol (days).	Time of action of CO_2 (days).
42·7	115·8	158·5	19·6	4	1	17·5	141·0	158·5	48·4	9	6
37·5	121·0	,,	22·4	5	2	14·2	144·3	,,	59·7	11	8
26·6	131·9	,,	31·9	7	4						

In the above tables bound $La^{\cdots}$ refers to lanthanum ions which are still balanced by chlorions. The unknown amount of carbonated lanthanum ion attached to the micelles is not included, but has been counted in with the un-ionised lanthanum. After standing for a year, the mixture from the above experiment was filtered and the solid washed, air-dried, and analysed. It consisted of well-formed rhombic plates and gave CO_2, 21·09%; loss on ignition, 45·10% [Calc. for $La_2(CO_3)_3,8H_2O$: CO_2, 21·94; loss on ignition, 45·85%]. The figures suggest that a small amount of hydroxide was still present.

Neodymium Hydroxide Sols.

Böhm and Niclassen (*Z. anorg. Chem.*, 1923, 132, 6) prepared a sol, described as having a beautiful blue colour, by peptising the hydroxide in hydrochloric acid. We have prepared and examined a number of such sols, starting from some very pure $Nd_2(C_2O_4)_3.10H_2O$ which had been prepared by the late Professor C. James (0·1255 G. gave on ignition 0·0574 g. of Nd_2O_3. Calc.: 0·0576 g.).

Apart from their blue colour, the neodymium sols are very similar to those of lanthanum in their general characteristics, and are equally sensitive to the action of carbon dioxide. They can be prepared by peptisation of the hydroxide with the chloride or, better, hydrochloric acid, and readily result, in a dilute form, by autopeptisation on washing the hydroxide precipitated by ammonia from chloride solution.

The following figures for sol 7 may be taken as typical of the results obtained with these sols. No strict precautions had been taken to exclude carbon dioxide. The rate of ageing was certainly much too great, and if carbon dioxide were rigidly excluded, there can be little doubt that these sols would be as stable as those of lanthanum hydroxide.

The " bound $Nd^{\cdots}$ " is that still balanced by chlorions and does not include any carbonated neodymium ions which may be attached to the micelles.

Total Nd.	Un-ionised Nd.	Bound $Nd^{\cdots}$.	Free $Nd^{\cdots}$.	Cl′.	n.	Age (days).
230	199	17·4	13·6	31·0	11·4	6
226	185·2	16·8	14·0	30·8	11·0	18
222	181·2	15·4	15·4	30·8	11·1	26
226	185·2	11·8	19·0	30·8	15·7	52
219	188·2	11·5	19·3	30·8	16·3	63
220	189·2	5·5	25·3	30·8	34·4	245

A very small crystalline deposit was obtained from this sol after 245 days, by which time all the sol had been used in analyses. This deposit still contained a trace of chloride but was free from carbonate. It seemed to consist of the hydroxide but may have been a basic chloride. The only optical measurement which could be made was that of the refractive index. The very small violet crystals were weakly birefringent and the values were practically the same as for the corresponding lanthanum crystals, *viz.*, about 1·71 and 1·73. The crystal system was probably either orthorhombic or monoclinic.

Thorium Hydroxide Sols.

These sols can be prepared either at room temperature by peptisation of the cold-precipitated hydroxide with a solution of thorium chloride or hydrochloric acid or by Desai's method (*Kolloid-Chem. Beih.*, 1928, 26, 357), in which a suspension of the hydroxide in water is kept near the boiling-point while dilute hydrochloric acid is added very gradually until a transparent sol is obtained, for which many hours may be needed: any water lost by evaporation should be replaced at intervals. The results are recorded in Table VI.

Sols 15 and 16 show that the same results are obtained whether thorium hydroxide is added gradually to the hot acid or *vice versa*. It is evident that thorium hydroxide sols are remarkably stable towards ageing or dilution whether they have been prepared by the hot or the cold process. The two methods of preparation do not give sols of identical character, however, as is shown by their very different behaviour towards added acid. All sols prepared by the hot process give a heavy precipitate when made 5N with regard to hydrochloric acid, whereas none of the sols prepared by the cold process does so. The precipitate obtained with the hot-process sols disappears on considerable dilution.

It does not seem possible to prepare by the cold process sols having high n values such as are normally obtained by the hot process. In order to confirm the striking result observed in sol 11, where the n value was as low as 1·15, a mixture was made from 10 c.c. of sol 12 and 10 c.c. of 0·38N-hydrochloric acid. This should give a sol with $n = 1·24$ if all the acid reacted and the final sol contained no free $Th^{\cdots\cdot}$ or $H^{\cdot}$. Analysis of the mixture after 1 day gave:

Total Th.	Un-ionised Th.	Bound $Th^{\cdots\cdot}$.	Free $Th^{\cdots\cdot}$.	$H^{\cdot}$.	Cl′.	n.
854	473·9	318·6	61·5	0·9	381	1·49

It thus appears that, in sols prepared by the cold process, the micelles behave towards acid in much the same way as did the original hydroxide used in preparing the sols. This result should be compared with that given by a mixture of 100 c.c. of sol 7, when 835 days old (see Table VI), with 10 c.c. of 0·2N-hydrochloric acid. Two days after mixing, analysis gave:

Total Th.	Un-ionised Th.	Bound $Th^{\cdots\cdot}$.	Free $Th^{\cdots\cdot}$.	$H^{\cdot}$, by $NaPO_3$ method.	$H^{\cdot}$, by glass electrode.	Cl′.	n.
127·7	105·7	11·0	11·0	9·6	10·0	31·6	9·6

and after 5 hours' heating at 90°, the mixture then being 4 days old, the results were:

127·7	102·8	11·3	13·6	6·7	—	31·6	9·1

The amount of acid added was sufficient to give 18 mg.-equivs./l. in the mixture, so it is evident that only about half of it had reacted with the micelles after 2 days at room temperature to give an equivalent amount of free $Th^{\cdots\cdot}$. Since the value of n has remained practically unaltered, it would seem that some solution of

TABLE VI.

Thorium hydroxide sols prepared by Desai's hot process.

Sol.	Total Th.	Un-ionised Th.	Bound Th^{****}.	Free Th^{****}.	$H^{\cdot}$.	Cl'.	n.	Age (days).
7	140·1	126·1	14·0	0	0·3	14·3	8·9	1
	—	—	—	0·3	—	—	—	3
	—	126·1	13·7	,,	0·3	—	9·2	7
	—	,,	13·8	0·2	—	—	9·1	53
	—	,,	13·2	0·8	0·3	—	9·5	835
8	240·1	219·9	19·6	0·6	0·7	20·9	11·2	2
	240·0	219·5	20·2	0·4	0·4	21·1	10·9	178
	250·5	229·0	21·2	0·3	,,	21·9	10·8	587
13	907·5	701·0	76·2	130·3	12	218·5	9·2	1
	,,	694·0	78·5	135·0	5	,,	8·9	19
	907·6	693·4	68·5	145·7	3·8	218·0	10·1	1178
14	730·0	638·7	89	2·3	0	91·3	7·2	1
	,,	,,	88	3·3	0	,,	7·3	28
(Sol 14. When 27 days old diluted 12·5 times)	730 (for actual figures ÷ 12·5)	,,	86·7	4·6	0	91·3	7·4	2 (from dilution)
15 *	439·4	368·0	53·6	18·4	0	71·4	6·9	1
[$Th(OH)_4$ added gradually to hot HCl]	,,	,,	53·9	17·5	0	,,	6·8	3
	,,	368·3	51·9	19·3	0·3	,,	7·1	74
	,,	,,	50·7	20·4	0·3	,,	7·3	94
	,,	368·2	50·4	20·8	0·2	,,	,,	506
16 *	451·5	381·9	51·6	18·0	0	69·6	7·4	2
[HCl gradually added to hot mixture of $Th(OH)_4$ and water]	,,	,,	53·6	16·0	0	,,	7·1	4
	,,	,,	55·4	14·2	0	,,	6·9	29
	,,	,,	51·9	17·7	0	,,	7·4	74
	,,	,,	49·4	20·2	0	,,	7·7	507

Thorium hydroxide sols prepared by the cold process.

(Sols 9, 10, 11 peptised by $ThCl_4$, sol 12 by 5N-HCl.)

9	1641	1271	370	0	0	370	3·43	3
10	2500	1685·2	794·8	20	1·8	816·6	2·12	2
11	2163	985·4	852·4	325·8	0·3	1178·2	1·15	2
12 †	1755	1372	383	0	0	383	3·58	1
	1709 ‡	1327·5	381·5	0	0	381·5	3·48	6

* "$H^{\cdot}$" results for sols no. 15 and 16 obtained by means of the glass electrode were 1·9 mg.-equivs./l. at 62 days in each case. Any effect of the 12·5-fold dilution on sol 14 is within the limit of experimental error.

† No free Th^{****} or $H^{\cdot}$ could be detected in sol 12 after 75 days' or after 100 days' ageing, nor were any of these ions liberated when the 6-days old sol was diluted 12·5 times even after the diluted sol had stood for 14 days.

‡ A small deposit had settled out after 6 days and this was not shaken up before the analysis.

the micelles as a whole has occurred. This supports the view that the micelles are of a liquid nature, and that the n value is determined by their bulk composition much more than by adsorption on their surface. Were the latter the case, then any marked increase in the free Th^{****} ion must have led to a reduction in the n value when all bound ions are assumed to be Th^{****} ions as in our calculations. This result would be obtained whether the additional free Th^{****} ions are supposed to come directly from the un-ionised substance of the micelle or from Th^{****} ions previously adsorbed on the surface and displaced by hydrions. In the calculation such displaced ions would be deducted from the total thorium to obtain the figure for un-ionised thorium and so would thorium equivalent to the bound hydrion.

It seems likely that hydrions bound to the micelles of these hot-process sols only react slowly with the substrate in view of the length of time for which a relatively high hydrion concentration can persist in such sols. The micelles may normally contain a proportion of bound hydrions for this reason (see p. 283). On heating the acid sol a small reduction in the n value does occur. This may well be due to changes in distribution between the two liquid phases (*i.e.*, liquid micelle and intermicellar fluid) owing to change of temperature, and the new value of n is closer to that of the sol when freshly prepared at 90—100°. The relative steadiness of n suggests that the micelles of sol 7 were almost adsorptively saturated in spite of the fact that the sol contained hardly any free Th^{****} or $H^{\cdot}$ ions.

Concentration of thorium hydroxide sols prepared by Desai's method causes a diminution of the n value due to some of the free thorium ion becoming bound. The micelles of the original sols were evidently not adsorptively saturated though very nearly so. The following experiments were performed in this connection.

Expt. I: (*a*) 50 c.c. of sol 13 when 14 days old were evaporated by gentle boiling to just under 20 c.c.; (*b*) 100 c.c. of sol 13 when 16 days old were similarly reduced to about 24 c.c. This method of evaporation was employed, as the sols had been produced by gentle boiling. The analyses gave:

	Total Th.	Un-ionised Th.	Bound Th^{****}.	Free Th^{****}.	$H^{\cdot}$.	Cl'.	n.
Original sol	907·5	694	78·5	135	5	218·5	8·8
(*a*)	2292	1763	215·4	314	22	551·4	8·2
(*b*)	3738	2857	345·4	523	33	901·4	8·3

The relatively large amount of $H^{\cdot}$ in the concentrated sols is probably connected with the very large amount of free thorium ion present. The glass-electrode result quoted on p. 300 shows that the determinations, made by the sodium metaphosphate method, are probably reliable.

Expt. II : 60 c.c. of sol 15 when 94 days old were evaporated by gentle boiling to 18 c.c. :

	Total Th.	Un-ionised Th.	Bound Th$^{\cdot\cdot\cdot\cdot}$.	Free Th$^{\cdot\cdot\cdot\cdot}$.	H$^{\cdot}$.	Cl$'$.	n.
Original sol	439·4	368·3	50·7	20·4	0·3	71·4	7·3
Conc. sol	1450	1215·8	185·7	48·5	1·4	235·6	6·55
,, ÷ 3·3	439·4	368·3	56·3	14·7	0·4	71·4	6·55

Expt. III : 20 c.c. of sol 7 when 835 days old were evaporated to dryness at room temperature over concentrated sulphuric acid. The glassy residue was somewhat hygroscopic, increasing in weight by 5% on exposure to air for 24 hours. It dissolved rapidly in water to a clear sol. After this had been curded with 5 c.c. of 0·5N-ammonium sulphate, the trace of thoria obtained from the filtrate with ammonia weighed only 0·0003 g., corresponding to 0·2 mg.-equiv. of free thorium per l. of the original sol. Another 20 c.c. of the sol analysed in exactly the same way without any evaporation gave 0·0011 g. of thoria, corresponding to 0·8 mg.-equiv. of free thorium per l. The drastic concentration effected in this experiment led to the binding of three-quarters of the free thorium and a reduction of the n value of the micelles from 9·5 to 9·1.

Coagulation of Thorium Hydroxide Sols.—0·01N-Solutions of the ions OH$'$, F$'$, IO_3', HCO_3', C_2O_4'', $Fe(CN)_6''''$, PO_4''', P_2O_7'''', and PO_3' coagulate the whole of the thorium from thorium hydroxide sols when added in amounts equivalent to, or slightly greater than, the total thorium ion present; SO_4'', S_2O_3'', $Fe(CN)_6'''$, $Co(CN)_6'''$ and citrate ions coagulate only the micelles in similar circumstances. Higher concentrations of BrO_3', S_2O_6'', and S_4O_6'' cause coagulation of the sols, and very high concentrations of Cl$'$, Br$'$, I$'$, ClO_3', ClO_4', and MnO_4' cause complete or partial coagulation but the curds disperse again readily on dilution.

The great efficiency of iodates has been noted by others. A rough determination has been made of the relative efficiencies of ClO_3', BrO_3', and IO_3' as precipitants for a thorium hydroxide sol containing 90 mg.-equivs./l. of total thorium with about one-tenth of that amount of free and bound thorium ion. Table VII gives the results, together with the corresponding figures for the precipitation of a thorium nitrate solution of concentration equal to that of the (free + bound) thorium ion in the sol. The relative solubilities of the barium salts are also shown. There is an obvious similarity in the three sets of figures, and the inference is that solubility is at least one of the factors in sol coagulation.

TABLE VII.

Precipitating ion.	Relative concn. of K salt required for precipitation of $Th(OH)_4$ sol.	$Th(NO_3)_4$ solution.	Relative solubility of Ba salts at 15°.
ClO_3'	190	>800	2290
BrO_3'	3·8	48	39·3
IO_3'	1	1	1

Crystalline Basic Thorium Chloride.—Approximately 20 g. or 17·3 c.c. (d 1·158) of thorium hydroxide sol No. 10, after 6 years' storage in a tightly corked flask, had deposited 0·463 g. of dense, strongly doubly refracting crystals. These consisted of minute prisms which showed straight extinction and had a tendency to form St. Andrew's crosses and other groups. The crystals were filtered off, washed with a small amount of cold water (by which they were unaffected), and air-dried (Found : Th, 63·66; Cl, 9·74; Th : Cl = 0·999. $[Th\{Th(OH)_4\}_3]Cl_4.10H_2O$ requires Th, 63·85; Cl, 9·76%; Th : Cl = 1·0).

The mother-liquor from which the crystals had separated was absolutely clear and transparent, but still behaved like a sol in giving a typical amorphous curd when treated with ammonium sulphate in amount equivalent to its chloride content. Analysis of the mother-liquor gave : total Th, 11·47; Cl, 2·43% and free Th$^{\cdot\cdot\cdot\cdot}$ (in the filtrate and washings from the ammonium sulphate coagulum), 0·45%. These figures correspond (in mg.-equiv./l.) to :

Total Th.	Un-ionised Th.	Bound Th$^{\cdot\cdot\cdot}$.	Free Th$^{\cdot\cdot\cdot\cdot}$.	H$^{\cdot}$.	Cl$'$.	n.
2290	1497·2	783·7	9·05	—	792·8	1·91

which should be compared with those for sol 10 in Table VI.

When the relative weights of crystalline solid and residual sol are considered, the analyses indicate that evaporation to the extent of about 4% by wt. must have occurred from the sol during the 6 years' storage.

It is noteworthy that the crystalline basic salt has a higher n value (= 3) than have the micelles of the sol from which it has separated.

The ultramicroscope showed the presence in the mother-liquor of only a very small proportion of very heavy particles with slow Brownian movement, and this liquor showed only a relatively weak Tyndall beam. It must be concluded, therefore, in view of the large total thorium content, that the micelles present are too small to cause appreciable scattering of light and hence do not show up in the ultramicroscope. The dissolved material is in a state intermediate between that of a typical sol and that of a crystalloidal solution.

The majority of the glass-electrode measurements recorded in this paper were made by Mr. H. S. Hallett of the National Institute for Research in Dairying. We express our thanks to him and to the Director of the

Institute, Professor H. D. Kay. We also thank Dr. H. Liebmann who made some of the earlier p_H measurements, Dr. P. White and Mr. C. C. Butler for some observations with the ultramicroscope, and Dr. T. H. Goodwin who took the *X*-ray powder photographs. The *X*-ray apparatus used had been purchased with the help of a generous grant from Imperial Chemical Industries.

THE UNIVERSITY, READING. [*Received, December 22nd,* 1941.]

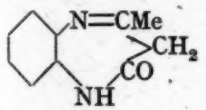
55. *The Condensation of* o-*Phenylenediamine with Ethyl Acetoacetate.*

By W. A. SEXTON.

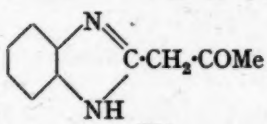
Under neutral or alkaline conditions *o*-phenylenediamine and ethyl acetoacetate afford a mixture of a *compound* having a seven-membered ring (I) and the isomeric *benziminazole-2-acetone* (II). Under acidic conditions ethyl β-2-aminoanilinocrotonate (III) is formed, and this cyclises to 2-methylbenziminazole.

IT has been shown by Coffey, Thomson, and Wilson (J., 1936, 856) that the condensation of ethyl acetoacetate with arylamines to give esters of β-arylaminocrotonic acids is favoured by acid catalysts. It was therefore of interest to investigate the effect of catalysts on the condensation of *o*-phenylenediamine with ethyl acetoacetate. It has now been observed that the formation of ethyl β-2-aminoanilinocrotonate (Hinsberg and Koller, *Ber.*, 1896, **29**, 1500) is conditioned by the presence of an acid catalyst. This was probably provided in the work of these authors by the use of unpurified ester in the condensation. Ethyl β-2-aminoanilinocrotonate exists in two forms, and although several recrystallisations of freshly prepared material failed to change the lower-melting (needle) form into the higher-melting (plate) form (Hinsberg and Koller, *loc. cit.*), a change in melting point occurred after a week, and the plate form was then obtained by one crystallisation. This change is probably a *cis-trans* isomerisation and may have been brought about by light.

In a solvent under neutral conditions, condensation affords a mixture of two substances, water and alcohol being eliminated. The first *compound* ($C_{10}H_{10}ON_2$) was formed in 71—72% of the theoretical



(I.)



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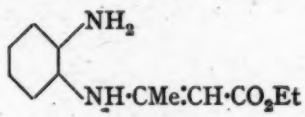

(III.)

yield. It gave a sparingly soluble sodio-derivative, was precipitated unchanged from its alkaline solution by acetic acid, and failed to couple with diazotised amines. Boiling 20% sulphuric acid brought about hydrolysis to 2-hydroxybenziminazole and acetone. Its constitution is therefore considered to be (I). Similar compounds containing seven-membered rings have been described by Thiele and Steimmig (*Ber.*, 1907, **40**, 955) and by Phillips (J., 1928, 2393), who treated *o*-phenylenediamine with acetylacetone and with malonic acid respectively.

The second (isomeric) substance (yield, 12—13%) is characterised by ready solubility in dilute alkali or acid and ability to couple with diazotised amines. These properties lead to the belief that the substance is *benziminazole-2-acetone* (II).

Attempts to cyclise ethyl β-2-aminoanilinocrotonate afforded only 2-methylbenziminazole, with elimination of ethyl acetate, thus confirming the observation of Hinsberg and Koller (*loc. cit.*). It therefore seems improbable that formation of (I) proceeds by elimination of alcohol from (III). It is more likely that the condensation of ethyl acetoacetate with *o*-phenylenediamine proceeds through aceto-acet-*o*-aminoanilide, which then cyclises under the conditions of the condensation to give (I) and (II). Reduction of *acetoacet-o-nitroanilide* with iron in fact gave (II), but formation of (I) in these circumstances was not detected.

EXPERIMENTAL.

Condensation of o-*Phenylenediamine with Ethyl Acetoacetate.*—(i) *Under acid conditions.* Powdered *o*-phenylenediamine (21·6 g.) was mixed with excess of ethyl acetoacetate purified as described by Coffey, Thomson, and Wilson (*loc. cit.*). After addition of three drops of hydrochloric acid the temperature rose to 35° and the mixture rapidly solidified. The ethyl β-2-aminoanilinocrotonate separated from light petroleum in white needle-shaped crystals (10·7 g.), m. p. 59—62°. After 8 days these had become yellow and melted at 85°. Recrystallisation from light petroleum then gave plates, m. p. 85°. Hinsberg and Koller (*loc. cit.*) give the m. p.'s of the two forms as 59° and 85°.

Unsuccessful attempts were made to cyclise the needle form of ethyl β-2-aminoanilinocrotonate to the compound (I) by (*a*) boiling in light petroleum solution in the presence of iodine, (*b*) heating to 100° either

alone, with 2N-hydrochloric acid, or with a trace of iodine. The iodine catalysed the formation of 2-methylbenziminazole.

(ii) *Under neutral conditions.* Purified ethyl acetoacetate (29 c.c.), mixed with xylene (20 c.c.), was added during ½ hour to a boiling solution of *o*-phenylenediamine (21·6 g.) in xylene (200 c.c.). The liquid was boiled for 1 hour, during which 50—60 c.c. were removed. The distillate had a lower aqueous-alcoholic layer. On cooling, the *compound* (I) (11·5 g.) separated in almost colourless needles, m. p. 120°; it crystallised from ethyl alcohol in colourless rhombohedra, m. p. 121° (Found: C, 69·5; H, 5·8; N, 16·05. $C_{10}H_{10}ON_2$ requires C, 69·0; H, 5·8; N, 16·1%).

After the separation of (I) the xylene mother-liquors were extracted with 10% sodium hydroxide solution (300 c.c.) and the crystals which separated were dissolved in water and acidified. This gave a further 7·0 g. of (I). In a second experiment the total yield of (I) amounted to 71·3% of the theoretical.

From the alkaline liquid, after the separation of the sodium salt of (I), acidification afforded *benziminazole-2-acetone*, which crystallised from water in needles or from benzene in prisms, m. p. 148° (Found: C, 69·0; H, 5·8; N, 15·8. $C_{10}H_{10}ON_2$ requires C, 69·0; H, 5·8; N, 16·1%).

(iii) *Under alkaline conditions.* The conditions of (ii) were repeated except that (*a*) the ethyl acetoacetate was rendered slightly alkaline by standing over solid sodium carbonate and (*b*) N/2-alcoholic potash (1 c.c.) was added to the xylene solution of *o*-phenylenediamine before addition of the ester. After reaction was complete benziminazole-2-acetone separated on cooling in hexagonal prisms (22 g.; 63·5%), m. p. 147°. The mother-liquor was extracted with 10% sodium hydroxide solution, and the extracts saturated with sodium chloride to precipitate the sodio-derivative of (I), which was then converted into (I) by acidification (6·5 g.; 18·5%). A further quantity of (I) (4·2 g.; 12%) was recovered by acidification of the aqueous mother-liquor.

Acetoacet-o-nitroanilide was prepared by condensation of ethyl acetoacetate with *o*-nitroaniline, and was separated from contaminants by solution in 2N-alkali and salting-out of the sodio-derivative. Acidification of the sodio-derivative gave the product (19% yield), which was crystallised from alcohol and then from benzene–light petroleum. It formed yellow-red prisms, m. p. 65° (Found: N, 12·3. $C_{10}H_{10}O_4N_2$ requires N, 12·6%).

A solution of acetoacet-*o*-nitroanilide (26·5 g.) in alcohol (120 c.c.), after addition of 3·5% hydrochloric acid (13 c.c.), was reduced by boiling for 5 hours with iron filings (36 g.). The liquid was neutralised, separated hot from the iron oxide, and the oxide washed with hot alcohol (30 c.c.). On cooling, benziminazole-2-acetone (0·5 g.) separated. Concentration of the mother-liquor gave three successive crops (total 14 g.) of material, m. p. 135—138° approx., identified as benziminazole-2-acetone. The residue after evaporation to dryness (6·6 g.) had m. p. 128—130° after crystallisation from benzene. The m. p. was not depressed by benziminazole-2-acetone.

The author wishes to thank Imperial Chemical Industries (Dyestuffs), Ltd., for permission to publish these results.

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BLACKLEY, MANCHESTER.

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56. *Reactions of Benzthiazole Derivatives. Part III. The Interaction of 1-Thiolbenzthiazoles and Alcohols.*

By W. H. DAVIES and W. A. SEXTON.

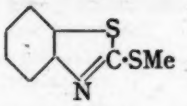
When heated with methyl or ethyl alcohol in the presence of catalysts, 1-thiolbenzthiazoles afford the benzthiazole derivatives (types I—IV) which it is suggested are derived by loss of H_2O, H_2S, or RSH from a labile hypothetical addition product (V) of the thiolbenzthiazole with the alcohol. The thermal isomerisation of *1-methoxybenzthiazole* to 2-methylbenzthiazolone is not catalysed by iodine.

These observations are considered in relation to the reactions of benzthiazole derivatives recorded in Parts I and II.

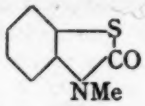
IT has previously been shown that methylation of 1-thiolbenzthiazole with methyl sulphate and aqueous sodium hydroxide gives mainly 1-methylthiobenzthiazole (I) and a small amount of 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (II) (Reed, Robertson, and Sexton, J., 1939, 473). An investigation has now been made of the alkylation of 1-thiolbenzthiazoles with methyl and ethyl alcohol in the presence of catalysts at elevated temperatures under pressure.

No appreciable reaction occurred on prolonged heating of 1-thiolbenzthiazole with methyl alcohol. In the presence of catalysts, however, in addition to gaseous by-products, (I, II, III, and IV) were obtained, the proportions depending on the catalyst and on the reaction conditions. With iodine as catalyst, (I, II, and IV) were identified, with bromine (II and IV) were obtained, whereas a single

experiment with sulphuric acid gave a 43% yield of (IV). The reaction between 1-thiolbenzthiazole and ethyl alcohol at elevated temperatures in the presence of iodine gave the ethyl analogue of (II),


(I.)

(II.)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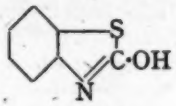

(IV.)

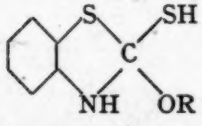
and (IV). 1-Thiol-4-methylbenzthiazole with methyl alcohol and iodine afforded 1-thio-2 : 4-dimethyl-1 : 2-dihydrobenzthiazole, and 4-chloro-1-thiolbenzthiazole under similar conditions gave 4-chloro-2-methylbenzthiazolone.

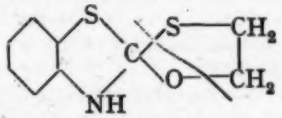
At the minimum temperature required for ensuring reaction in a reasonable time between 1-thiolbenzthiazole and methyl alcohol in the presence of iodine, a high proportion of (I) was formed. Increasing the temperature or the period of heating increased the proportion of (II) at the expense of (I) and it seems probable that (II) arises by the thermal rearrangement of (I) (Reed, Robertson, and Sexton, *loc. cit.*).

The formation of 1-hydroxybenzthiazole (IV) was less dependent on the reaction time and temperature. It was not formed by hydrolysis of the other products, since it could not be isolated from the reaction products of 1-thiolbenzthiazole, 1-methylthiobenzthiazole (I) or 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (II) with water in the presence of iodine or from the reaction product of (I) with aqueous methyl alcohol containing iodine.

As the production of 1-alkoxybenzthiazoles might have been expected in this reaction, the thermal stability of 1-*methoxybenzthiazole* was examined. Oxidation of methyl phenylthioncarbamate with potassium ferricyanide by the method of Hunter and Parken (J., 1935, 1755) gave a mixture of unchanged ester and 1-methoxybenzthiazole. The latter was more conveniently obtained by treating 1-chlorobenzthiazole with alcoholic sodium methoxide (cf. Hofmann, *Ber.*, 1880, **13**, 10) and its properties do not accord with those ascribed to 1-methoxybenzthiazole by Hunter and Parken (*loc. cit.*). Their proof of structure, namely, by bromination to 5-bromo-1-methoxybenzthiazole, is, however, invalid, since bromine might effect simultaneous oxidation and bromination of methyl phenylthioncarbamate itself to give 5-bromo-1-methoxybenzthiazole. Confirmation of the structure of our methoxybenzthiazole was afforded by its thermal isomerisation to 2-methylbenzthiazolone, which took place at a much lower temperature than that required for the corresponding thio-derivative (I). It therefore appears that, if methoxybenzthiazoles were formed in the reaction between thiolbenzthiazoles and methyl alcohol, they would be isomerised under the conditions of the reaction. No reaction took place when 1-hydroxybenzthiazole (IV) was heated with methyl alcohol in the presence of iodine.

The evidence suggests that the various products are formed from a labile addition product (V) of 1-thiolbenzthiazole and the alcohol ROH by loss of H_2O, H_2S, or RSH, together with the isomerisation

(V.) 


(VI.)

known to be possible under the experimental conditions. Such a mechanism also explains the thermal conversion of 1-β-hydroxyethylthiobenzthiazole into 1-hydroxybenzthiazole (Sexton, J., 1939, 470), the first step being the formation of an unstable intermediate (VI).

Although 1-methoxybenzthiazole is readily isomerised by heat, this reaction is not catalysed by iodine, in contrast to the isomerisation of the analogous thio-derivatives (Reed, Robertson, and Sexton, *loc. cit.*). This suggests that the action of iodine or methyl iodide as catalyst in the isomerisation of the thio-compounds proceeds by addition first to the sulphur atom of the alkylthio-group, giving a sulphonium compound, which eliminates the catalyst after rearrangement to a quaternary ammonium salt (compare Parts I and II).

Experimental.

(1) *Reaction of* 1-*Thiolbenzthiazole with Methyl Alcohol.*—The reaction mixtures were extracted with aqueous sodium hydroxide to remove 1-thiolbenzthiazole (m. p. 179°) and 1-hydroxybenzthiazole (IV) (m. p. 138°), which were liberated on acidification. Treatment of the alkali-insoluble material with concentrated hydrochloric acid (4—5 vols.) extracted 1-methylthiobenzthiazole (I) (m. p. 50°), which was isolated after basification, and left the 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (II) (m. p. 90°), which has no basic properties. In all cases, the yields given are of unpurified fractions obtained in this way, though these were purified when it was necessary to ensure their identity. Identification was by mixed m. p. with authentic materials prepared by the methods described in Parts I and II.

(a) *Without catalyst.* 1-Thiolbenzthiazole (16·7 g.) and methyl alcohol (8 c.c.) were heated in a sealed tube at 210—215° for 10 hours. 1-Thiolbenzthiazole (14·7 g.), m. p. 172—176°, was recovered.

(b) *With iodine as catalyst.* 1-Thiolbenzthiazole (334 g.), methyl alcohol (128 g.), and iodine (0·8 g.) were stirred in an electrically heated autoclave. The results are summarised below:

		Products.					
		(I.)		(II.)		(IV.)	
Temp.	Time, hours.	Wt., g.	M. p.	Wt., g.	M. p.	Wt., g.	M. p.
150° *	3	143	34—36°	—	—	—	—
150	10	273	43—48	—	—	57	115—125°
175	3	224	32—34	53·2	84—86°	35·7	126—128
175	10	116	semi-solid	115	75—82	45·7	122—133
200	4	80	semi-solid	166	50—68	55	127—129
225	3	40	semi-solid	204·5	48—51	36·5	114—128

* In this experiment alone, 1-thiolbenzthiazole (181 g.) was recovered unchanged.

After 1-thiolbenzthiazole (334 g.) had been heated with methyl alcohol (96 g.) and iodine (0·8 g.) in the autoclave for 10 hours at 150°, the products were (I) (239 g.), m. p. 39—42°, (II) (19·4 g.), m. p. 86—90°, and (IV) (61 g.), m. p. 118—128°. From a mixture of 1-thiolbenzthiazole (167 g.), methyl alcohol (128 g.), and iodine (0·8 g.) heated at 150° for 10 hours, the products obtained were (I) (109 g.), m. p. 38—45°, and a mixture of (IV) with unchanged 1-thiolbenzthiazole (47·2 g.) which was not separated.

(c) *With bromine as catalyst.* In a sealed tube at 200° 1-thiolbenzthiazole (22·2 g.), methyl alcohol (8·6 g.), and bromine (0·2 g.) afforded after 10 hours 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (II) (5·0 g.), m. p. 82—85°, and 2-methylbenzthiazolone (III) (10·0 g.), m. p. 74—76° after one crystallisation from methyl alcohol.

(d) *With sulphuric acid as catalyst.* Under the same conditions as (c), 1-thiolbenzthiazole (22·2 g.), methyl alcohol (8·6 g.), and sulphuric acid (a few drops) gave 1-hydroxybenzthiazole (IV) (8·1 g.), m. p. 130—135° after one crystallisation from methyl alcohol. 1-Methylthiobenzthiazole was isolated from the residue after separation of the alkali-soluble material. The products were not further examined.

(e) *Miscellaneous experiments bearing on the mechanism.* The reactants were heated in sealed tubes at 210—215° for 10 hours: the products were isolated as before.

(i) From 1-hydroxybenzthiazole (10 g.), methyl alcohol (5·4 c.c.), and a trace of iodine, 1-hydroxybenzthiazole (9·5 g.), m. p. 125—134°, was recovered.

(ii) From 1-methylthiobenzthiazole (10 g.), water (2 c.c.), and a trace of iodine, 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (2·5 g.), m. p. 86—90°, was formed and 1-methylthiobenzthiazole (5·8 g.), m. p. 36—42°, was recovered. No appreciable amount of alkali-soluble solid was isolated.

(iii) From 1-methylthiobenzthiazole (10 g.), methyl alcohol (1·2 c.c.), water (0·8 c.c.), and a trace of iodine, 1-thio-2-methyl-1 : 2-dihydrobenzthiazole (1·2 g.), m. p. 82—87°, was formed and 1-methylthiobenzthiazole (6·4 g.), m. p. 40—50°, was recovered. No appreciable amount of alkali-soluble material was isolated.

(iv) 1-Thio-2-methyl-1 : 2-dihydrobenzthiazole (9 g.), after being heated with water (2 c.c.) and a trace of iodine, was recovered (8·8 g.), m. p. 89—90°.

(v) From 1-thiolbenzthiazole (16·7 g.), water (5 c.c.), and a trace of iodine, the initial material was recovered (15·6 g.), m. p. 173—177°.

(2) *Reaction of 1-Thiolbenzthiazole with Ethyl Alcohol.*—1-Thiolbenzthiazole (22·4 g.), ethyl alcohol (12·6 g.), and iodine (0·07 g.) were heated in a sealed tube at 230° for 10 hours. The products, separated as in the experiments with methyl alcohol, were 1-hydroxybenzthiazole (5·3 g.), m. p. 100—110°, raised to 139—140° by two crystallisations from alcohol, and 1-thio-2-ethyl-1 : 2-dihydrobenzthiazole (15·5 g.), m. p. 76° after one crystallisation from alcohol.

In a second experiment with double the quantity of iodine, the yield of 1-thio-2-ethyl-1 : 2-dihydrobenzthiazole was 18·5 g., and of 1-hydroxybenzthiazole 2·8 g.

(3) *Reaction of Substituted 1-Thiolbenzthiazoles with Methyl Alcohol.*—(a) *4-Chloro-1-thiolbenzthiazole.* The thiol (20·2 g.) was heated in a sealed tube with methyl alcohol (6·5 g.) and iodine (0·1 g.) for 10 hours at 230°. The product was partly liquid and partly a reddish-brown solid. The latter, after being washed with dilute sodium hydroxide solution and crystallised from alcohol, was identified by m. p. 109—110° and mixed m. p. as 4-chloro-2-methylbenzthiazolone.

(b) *1-Thiol-4-methylbenzthiazole.* Treated as in (a), this gave a solid product only, which after crystallisation from alcohol was identified by m. p. 190° and mixed m. p. as 1-thio-2 : 4-dimethyl-1 : 2-dihydrobenzthiazole.

(4) *1-Methoxybenzthiazole.*—(a) Methyl phenylthioncarbamate (4·3 g.), dissolved in 30% aqueous sodium hydroxide (37 c.c.) containing methyl alcohol (5 c.c.), was diluted with water (87 c.c.) and added in 10 c.c. portions at 5-minute intervals to a stirred solution of potassium ferricyanide (30 g.) in water (140 c.c.) at 80—85°. After a further 10 minutes' stirring, the oil was separated, dissolved in a little light petroleum (b. p. 40—60°), and filtered from insoluble red tar. The solvent was removed, and the residual reddish oil crystallised from a little methyl alcohol with good cooling. The product, m. p. 31—33°, had a characteristic

odour of wintergreen. Treatment of the alkaline aqueous layer with ether extracted crude methyl phenylthioncarbamate, m. p. 82—90° (mixed m. p. with an authentic specimen 89—93°). Hunter and Parken (*loc. cit.*) give the m. p. of " 1-methoxybenzthiazole " as 88—89° (the m. p. of pure methyl phenylthioncarbamate is 93°).

(b) 1-Chlorobenzthiazole (16·9 g.) was added to a solution of sodium methoxide (sodium 2·4 g., in methyl alcohol, 40 c.c.), the mixture boiled for 3 hours and poured into water, and the solid obtained crystallised from methyl alcohol with good cooling; it had m. p. 34—35°; yield, 11 g. (Found: C, 58·0; H, 4·1; N, 8·4; S, 19·5. C_8H_7ONS requires C, 58·2; H, 4·3; N, 8·5; S, 19·4%). The substance had the same wintergreen type of smell as the product obtained in (a) and the mixed m. p. of the two products was 32—34°.

(5) *Isomerisation of* 1-*Methoxybenzthiazole.*—After heating for 3 hours at 150°, with or without a trace of iodine, unchanged material, m. p. 33—35°, was recovered. After heating at 175—180° for 3 hours, the product (in absence of iodine) readily solidified on cooling to give 2-methylbenzthiazolone, m. p. and mixed m. p. 74—75°; in presence of a trace of iodine, the product was a mixture of oil and 2-methylbenzthiazolone, m. p. and mixed m. p. 73—75°.

The authors thank Imperial Chemical Industries (Dyestuffs), Ltd., for permission to publish these results.

Research Laboratories, I.C.I. (Dyestuffs), Ltd.,
Blackley, Manchester.

[*Received, December* 12*th*, 1941.]

NOTES.

The Determination of Hypophosphites by Potassium Permanganate. By James R. Pound.

The usual methods for the determination of hypophosphites suffer from various disadvantages. Oxidation of the hypophosphite is slow both by hypobromite and by bromate–bromide in slightly acid solution, there is danger of loss of bromine, and the solutions must be standardised frequently and under the same conditions as the test; potassium permanganate may be used instead of the bromate; and all three methods are completed by addition of potassium iodide and titration by sodium thiosulphate. In our experiments the hypobromite method tends to give higher results than the other two, but, carefully used, all three methods agree with the well-known mercuric chloride method, in which the resulting mercurous chloride is weighed; the last method requires about 4 hours' treatment on the water-bath or a longer time in the cold. Oxidation of hypophosphite to phosphate by repeated evaporation with nitric acid is slow but is accurate if the phosphate is subsequently weighed as magnesium ammonium phosphate hexahydrate.

Oxidation of hypophosphite by potassium permanganate in neutral or acid solution is slow, and direct titration is impossible. Even after several days' standing, oxidation in acid solution does not exceed 96%; however, a *small* amount of potassium bromide has a catalytic effect, possibly due to the formation of free bromine, and oxidation is complete in a few hours at room temperature. To 5 ml. of (approx.) N/10-hypophosphite, in a glass-stoppered flask, there are added (in order) 10 ml. of N/10-permanganate, 0·5—1 ml. of 10N-sulphuric acid, and 0·1 ml. of M-potassium bromide; after 2—3 hours' standing, 10 ml. of N/10-ferrous sulphate (freshly standardised) are added and the flask is immediately closed and shaken; the brown oxides of manganese are soon dissolved and the small amount of bromine vapour is fixed; then the excess of ferrous sulphate is titrated by the permanganate solution. The errors involved in thiosulphate–iodine work are certainly not less than in this process. As the potassium bromide and bromine concentrations in the solution are always low, there is little bromine in the flask at any time and therefore little tendency to loss of bromine; however, the stoppers of the flasks should be lightly vaselined. According to the equation for this action 10 ml. of N/10-potassium permanganate require 0·2 ml. of 10N-acid and 1 ml. of M-potassium bromide, so the smaller volume of bromide used indicates its catalytic effect. Excess of acid should be avoided, as decomposition of the potassium permanganate and loss of oxygen may then occur, especially in the presence of the manganese oxides produced.

In one series of experiments the above method gave the normality of the hypophosphite solution as 0·1172 (the same value being found by the phosphate method), and the error was ± 1·4% (six determinations over periods of 2—70 hours); in another series of seven experiments, with 3 hours' to 3 days' standing, the error was ± 1%. It is difficult to obtain this accuracy with any of the other volumetric methods, even working with careful " blanks ".

The author thanks Mr. E. Mann for confirmatory estimations.—The School of Mines, Ballarat, Victoria, Australia. [*Received, December* 17*th*, 1941.]

Preparation of Some p-*Alkyl-substituted Benzoic Acids.* By A. Zaki and H. Fahim.

A solution of the *n*-alkylbenzene (prepared from bromobenzene by the Fittig reaction) and acetyl chloride in light petroleum (b. p. 60—70°) at 0° was treated with aluminium chloride, stirred for 1 hour at room temperature, heated on the water-bath for ½ hour, and decomposed by ice-cold water. Oxidation of the resulting

p-alkylphenyl methyl ketone to the acid was effected by alkaline sodium hypobromite solution (sodium hydroxide, 25 g.; water, 70 c.c.; ice, 60 g.; bromine, 10 c.c.). The yields of the acids were nearly quantitative.

On oxidation with potassium permanganate, the *p*-alkylbenzoic acids gave terephthalic acid (methyl ester, m. p. 140°).

p-*n*-Butylphenyl methyl ketone, obtained in 55% yield by the action of acetyl chloride (32 g.) and aluminium chloride (32 g.) on *n*-butylbenzene (Braun and Deutsch, *Ber.*, 1912, **45**, 2181) (20 g.) in light petroleum (50 c.c.), was a slightly yellow liquid, b. p. 268—270°/766 mm. The *oxime* separated from dilute methyl alcohol in white crystals, m. p. 43—44° (Found: C, 75·5; H, 8·9; N, 7·3. $C_{12}H_{17}ON$ requires C, 75·4; H, 8·9; N, 7·3%), the *semicarbazone* from alcohol in white star-like crystals, m. p. 182—183° (Found: C, 67·1; H, 8·2; N, 18·05. $C_{13}H_{19}ON_3$ requires C, 66·95; H, 8·15; N, 18·0%), and the p-*nitrophenylhydrazone* from alcohol in tiny orange-yellow crystals, m. p. 151—152° (Found: C, 69·8; H, 7·1; N, 13·9. $C_{18}H_{21}O_2N_3$ requires C, 69·45; H, 6·75; N, 13·5%).

p-n-*Butylbenzoic acid* was obtained by shaking *p*-*n*-butylphenyl methyl ketone (3·5 g.) with warm sodium hypobromite solution (87 c.c.) for ½ hour. The product was diluted with water, and the acid precipitated with sulphur dioxide. It crystallised from dilute alcohol in white needles, m. p. 101° (Found: C, 74·1; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·85%).

p-*n*-Amylphenyl methyl ketone, obtained in 50% yield by the action of acetyl chloride (20 g.) and aluminium chloride (20 g.) on *n*-amylbenzene (Schramm, *Annalen*, 1883, **218**, 389) (15 g.) in light petroleum (50 c.c.), was a yellowish oil, b. p. 145°/11 mm. The *oxime* separated from dilute alcohol in tiny white needles, m. p. 62—63° (Found: C, 75·7; H, 9·2; N, 6·7. $C_{12}H_{19}ON$ requires C, 76·1; H, 9·3; N, 6·8%), the *semicarbazone* from alcohol in tiny white needles, m. p. 180—181° (Found: C, 68·0; H, 8·3; N, 17·3. $C_{14}H_{21}ON_3$ requires C, 68·0; H, 8·5; N, 17·0%), and the p-*nitrophenylhydrazone* from alcohol in orange needles, m. p. 149—150° (Found: C, 70·0; H, 7·0; N, 13·0. $C_{19}H_{23}O_2N_3$ requires C, 70·15; H, 7·1; N, 12·9%).

p-n-*Amylbenzoic acid*, obtained as above by shaking *p*-*n*-amylphenyl methyl ketone (4 g.) with sodium hypobromite solution (100 c.c.) for ½ hour, crystallised from dilute alcohol in white scales, m. p. 88° (Found: C, 74·95; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

p-*n*-Hexylphenyl methyl ketone, obtained in 68% yield by the action of acetyl chloride (50 g.) and aluminium chloride (50 g.) on *n*-hexylbenzene (Braun and Deutsch, *loc. cit.*) (40 g.) in light petroleum (100 c.c.), was a yellowish oil, b. p. 158°/12 mm. The *oxime* separated from dilute alcohol in white crystals, m. p. 45—46° (Found: C, 76·7; H, 9·5; N, 6·3. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·6; N, 6·4%), the *semicarbazone* from alcohol in white crystals, m. p. 178° (Found: C, 69·1; H, 9·0; N, 16·2. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%), and the p-*nitrophenylhydrazone* from alcohol in orange feathery crystals, m. p. 135° (Found: C, 70·7; H, 7·4; N, 12·3. $C_{20}H_{25}O_2N_3$ requires C, 70·8; H, 7·4; N, 12·4%).

p-n-*Hexylbenzoic acid*, obtained by shaking *p*-*n*-hexylphenyl methyl ketone (4 g.) with sodium hypobromite solution (100 c.c.) for 1½ hours, separated from dilute alcohol in white crystals, m. p. 97° (Found: C, 75·9; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

p-*n*-Heptylphenyl methyl ketone, obtained in 69% yield by the action of acetyl chloride (28 g.) and aluminium chloride (28 g.) on *n*-heptylbenzene (Sabatier and Mailhe, *Compt. rend.*, 1914, **158**, 834) (20 g.) in light petroleum (50 g.), was a yellowish oil which darkened on keeping, b. p. 160—163°/7 mm. The *oxime* separated from dilute alcohol in white crystals, m. p. 41—42° (Found: C, 77·2; H, 10·0; N, 5·8. $C_{15}H_{23}ON$ requires C, 77·25; H, 9·9; N, 6·0%), the *semicarbazone* from alcohol in white crystals, m. p. 176° (Found: C, 70·5; H, 9·1; N, 15·15. $C_{16}H_{25}ON_3$ requires C, 70·5; H, 8·9; N, 14·9%), and the p-*nitrophenylhydrazone* from alcohol in tiny orange needles, m. p. 140° (Found: C, 71·4; H, 7·6; N, 12·0. $C_{21}H_{27}O_2N_3$ requires C, 71·4; H, 7·65; N, 11·9%).

p-n-*Heptylbenzoic acid*, obtained by shaking *p*-*n*-heptylphenyl methyl ketone (15 g.) with sodium hypobromite solution (750 c.c.) for 3 hours, separated from dilute alcohol in white crystals, m. p. 101·5° (Found: C, 76·3; H, 9·1. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%).

p-*n*-Octylphenyl methyl ketone, obtained in 61% yield by the action of acetyl chloride (62 g.) and aluminium chloride (62 g.) on *n*-octylbenzene (von Schweinitz, *Ber.*, 1886, **19**, 641) (40 g.) in light petroleum (100 c.c.), was a yellowish oil, b. p. 165—168°/4 mm. (cf. Lipinski, *Ber.*, 1898, **31**, 938). The oxime separated from dilute alcohol in white crystals, m. p. 52—53° (Lipinski, *loc. cit.*, gives m. p. 43°) (Found: C, 77·7; H, 10·2; N, 5·9. Calc. for $C_{16}H_{25}ON$: C, 77·7; H, 10·1; N, 5·7%), the *semicarbazone* from alcohol in white needles, m. p. 174° (Found: C, 70·6; H, 9·3; N, 14·5. $C_{17}H_{27}ON_3$ requires C, 70·6; H, 9·3; N, 14·5%), and the p-*nitrophenylhydrazone* from alcohol in yellow needles, m. p. 127° (Found: C, 71·8; H, 8·0; N, 11·7. $C_{22}H_{29}O_2N_3$ requires C, 71·9; H, 7·9; N, 11·4%).

p-*n*-Octylbenzoic acid, prepared by shaking *p*-*n*-octylphenyl methyl ketone (8 g.) with sodium hypobromite solution (750 c.c.) for 2 hours, separated from dilute alcohol in white crystals, m. p. 99—100° (Beran, *Ber.*, 1885, **18**, 139, gives m. p. 139°) (Found: C, 76·8; H, 9·4. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·4%).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, October 24th*, 1941.]

THE HUNDRED AND FIRST ANNIVERSARY MEETING.

THE Annual General Meeting was held at Burlington House on Thursday, 26th March, 1942, at 12 noon. The President, Dr. W. H. Mills, F.R.S., occupied the Chair.

The notice convening the meeting was read.

The Report of Council for 1941 was presented, and Dr. C. W. Davies the senior Secretary, in introducing the general sections of the Report, referred to the action taken in sending out of London the duplicate volumes of Journals published earlier than 1920. This had caused little inconvenience to borrowers, and it was satisfactory to know that a large number of volumes most difficult to replace would not be endangered by further air raids on London. He also paid a tribute to Mr. Carr and the depleted staff for their success in keeping the business of the Society moving smoothly during a very difficult year. In particular, the prompt dispatch of the Society's publications was subject to recurring difficulties, some of which were outside the control of the Editors or Mr. Carr, and it was only by constant effort that the inevitable delays had been minimised.

The Treasurer, who was then called upon by the President to deal with the accounts, stated that the most significant feature of the year's accounts was the increase in subscriptions of £587 16*s.* 2*d.* above those received in 1940; this was due to the co-operation scheme, which though launched in war time—late in 1939—had made a good start. The following table shows the variation in number of Fellows and the subscriptions received since 1926, which was the peak year:—

Year	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941
Membership	4093	4040	3980	3925	3840	3775	3608	3620	3628	3725	3746	3775	3799	3773	3695	4516
Subscriptions in £	9910	9909	9827	9521	9448	9134	8598	8757	8945	8934	8922	8888	8994	8809	8503	9091

The subscriptions given in any year are those received in that year for the current year, past years and in advance for the coming year. While the amount received for 4516 members is £819 less than in 1926, yet the cost of each co-operation member to the Society is less, as there is a limit to the number of publications received. Also in 1933 was instituted the new scheme of Fellows paying 30*s.* and likewise receiving fewer publications.

According to the co-operation agreement, after deducting such monies as are due to the Institute of Chemistry, the balance has been divided equally between the Chemical Society and the Society of Chemical Industry. This is only a just division in the unlikely event of the cost of publications supplied by the two Societies to co-operative members being the same, and the Chemical Council has set up a Committee consisting of the Officers of the Chemical Council, the Treasurers of the three bodies, Dr. J. J. Fox, and Dr. H. J. T. Ellingham, to examine the effect of the scheme on the finances of the two publishing societies. The reason for the inclusion of Dr. Ellingham on the Committee is that originally Dr. Brady, Dr. Ellingham, Dr. Lampitt and Mr. Davidson Pratt advised the Chemical Council on the details of the scheme, and Dr. Ellingham was largely responsible for the calculations on which the scheme was based. The Treasurer felt that we were greatly indebted to these Fellows for the successful foundations which they had laid. Any inequalities in the division of the subscriptions between the two Societies will be eventually adjusted.

The 30*s.* Fellowship Scheme appears to be meeting with success as the percentage of resignations is not unduly high. The statistics are as follows:—

30*s.* Fellows 1933—41.

Total Elected.	Resigned before Transfer to Full Fellowship.	Resigned on Transfer.	Transferred to Full Fellowship.	Resigned since Transfer.	Present Number of 30*s.* Fellows.
793	49	91	192	40	421

The main increase in expenditure for the year is that due to War Damage Insurance, amounting to £699 17*s.* 6*d.*, and the total abnormal expenditure after including the sums shown under Air Raid Precautions is over £1000. Nevertheless after putting to the Special Reserve Fund a sum of £1800 as against £1100 in 1940 for publications the deficit on the year's working is reduced from £403 10*s.* 11*d.* to £187 19*s.* 11*d.*

A new fund, the Quinquennial Index Fund, has been instituted to provide for the Chemical Society's share of the cost of the next Quinquennial Index of the Abstracts. Into that fund will be paid any sums received from the Bureau from sales of the two indexes already published by them and such sums as the Council may decide year by year to transfer thereto. The Bureau, which is responsible for the accounts for Section AIII, has been able to put £700 to reserve so as to provide for post war eventualities.

The Treasurer stated that the Society owed special thanks to its representatives on the Bureau, as many wartime problems requiring careful consideration had had to be met.

Finally he paid tribute to the staff and to Mr. Carr and Mr. Morris in particular, who in spite of working in London and Oxford, respectively, had overcome the inherent difficulties.

The adoption of the Report of Council for 1941, including Statements of Accounts and Balance Sheets, was proposed by Professor H. T. S. Britton, seconded by Dr. A. E. Gillam and carried unanimously.

The names of Fellows elected to vacancies on the Council were declared as follows :—

President : Dr. W. H. Mills.

Vice-Presidents, who have not filled the office of President : Dr. Francis H. Carr, Professor Alexander Findlay, Professor C. S. Gibson, Professor W. N. Haworth.

Elected Ordinary Members of Council :

Constituency I. South-East England.
Dr. D. J. G. Ives.
Dr. F. B. Kipping.
Dr. H. W. Thompson.

Constituency II. Central and South-West England and South Wales.
Dr. G. S. Hartley.
Dr. E. B. Maxted.
Dr. H. B. Watson.

Constituency III. North-West England, North Wales and the Isle of Man.
Dr. F. Fairbrother.
Dr. E. H. Rodd.

Constituency IV. North-East England.
Dr. J. W. Baker.

The Report of the Scrutators on the ballot for the election of an Elected Ordinary Member of Council for Constituency V. (Scotland) was received, and Professor J. W. Cook was declared elected.

A Vote of Thanks to the Vice-Presidents, Treasurer, Honorary Secretaries, Council and Committees for their services during the past year, proposed by Dr. J. W. Baker and seconded by Dr. E. G. V. Percival was carried unanimously and acknowledged by Dr. H. J. T. Ellingham.

On the motion of Dr. J. D. M. Ross, seconded by Mr. D. O. Jordan, Messrs. W. B. Keen & Co., were appointed Auditors for 1942.

The Meeting was then adjourned.

A Luncheon at which 63 Fellows and their guests were present, was held at Stewarts' Restaurant at 1 p.m.

On the resumption of the Meeting at 2.30 p.m., the President said that this was the first Annual General Meeting of the Society since the entry of the United States of America into the War. He was sure that Fellows would agree that it was appropriate and desirable that they should make it the occasion of a cordial message of greeting to the American Chemical Society. He then asked Fellows present to signify their approval of the following cable :—

> The Chemical Society Hundred and First Annual General Meeting to-day send hearty greetings to American Chemical Society and express their earnest hope that the united efforts of the allied nations may achieve early victory.

This was dispatched during the meeting.

The President then stated : " Our next business is the presentation of the Longstaff Medal. Dr. G. D. Longstaff, a physician, was a generous benefactor to this Society; we owe to him a munificent bequest which formed the nucleus of The Research Fund, and with this bequest he associated the stipulation that a gold medal of not less value than £20 be awarded triennially to the Fellow of the Society, who, in the opinion of the Council, has done the most to promote chemical science by research. The first medal was presented in 1881, and this is the twenty-first award."

" On this occasion, the Council have awarded the medal to Professor Hugh Stott Taylor who holds the Chair of Physical Chemistry in the University of Princeton. Professor Taylor is chiefly distinguished for his extensive and important researches on adsorption and heterogeneous catalysis. He was probably the first to discover the presence of active centres in heterogeneous catalysts, and has been particularly successful in investigating the connection between heterogeneous catalysis and adsorption phenomena. He has taken a leading part in developing the theory of activated adsorption (or ' chemisorption '), and has also carried out, or directed, numerous researches in other branches of physical chemistry, as in

photochemistry and in reaction-kinetics as well as on the preparation of deuterium oxide. Under present circumstances he is naturally unable to be present to receive the medal in person, but has asked Professor Rideal, a very old friend of his, to receive it on his behalf."

On receiving the medal, Professor Rideal said that he gladly fulfilled Professor Taylor's wish that he should receive the Longstaff Medal on his behalf. Indeed it gave him a very definite pleasure in being a participant at this function. Some might wonder why Professor Taylor had chosen him. The explanation was a simple one. During the last War when invalided back from France, Profeessor Taylor and he had investigated catalytic hydrogen production and had thus had ample opportunity for days and nights of discussion. From this association " Catalysis in Theory and Practice " had emerged and there was born a friendship and mutual esteem which in spite of some differences in opinion had lasted and had grown stronger in the intervening period of almost a quarter of a century. Professor Taylor had sent him a cablegram in which he wished him to express the grateful appreciation of his American colleagues and the Princeton authorities whose support had made the work possible, and had offered the £20 to the Research Fund. Professor Rideal felt that if longer cables had been permitted, Professor Taylor would have enlarged upon this question of research which he evidently had so much in mind.

Professor Rideal added that our junior Fellows could be quite certain that there would be many opportunities for winning Longstaff Medals in the future in the subject of heterogeneous catalysis. If asked what aspect of the subject was important he would have said from the scientific point of view, all; from the material point of view, coal. Professor Taylor, as was well known, was now contributing to the catalytic chemistry of the hydrocarbons, the native raw material of the United States. Here in this country coal was almost our only native source of chemicals, and whilst the aromatic side of our chemical industry was provided for, thanks to the enterprise of our gasification industry, it was a national weakness that the other half of a well balanced chemical organisation, namely the aliphatic chemical industry, had hitherto been ignored. There were many ways in which this might be developed, through carbide or through hydrocarbon or methanol synthesis. Developed it must be, and in each step catalysis would intrude. The work of the recipient of the Longstaff Medal had pointed the way; it was for us to take it.

In presenting the Harrison Memorial Prize for 1941 to Dr. H. N. Rydon, the President said that in making this award, the Electors had been impressed by his work on unsaturated compounds—particularly by the contribution he had made to our knowledge of the Michael reaction. They had also appreciated his share in investigations on the mobility of hydrogen in ethylene compounds by observation of isotopic exchange and had recognised the merit of his simple but elegant syntheses of degradation products from terpenes, and the value of his work, done in collaboration with Sir Robert Robinson, on nor-œstrone. The President added that on becoming a Harrison prizeman Dr. Rydon had joined a distinguished company which would prove a great incentive to him.

In receiving the medal, Dr. Rydon expressed his high appreciation of the honour and his debt of gratitude to all those with whom he had been associated in his research work, and especially to the late Sir Jocelyn Thorpe.

The President then delivered the Eighth Pedler Lecture entitled: "The Basis of Stereochemistry."

At the conclusion, a Vote of Thanks to him for his services in the Chair and for his lecture was proposed by Dr. J. Kenyon, seconded by Dr. E. E. Turner, and carried with acclamation.

REPORT OF COUNCIL, 1941.

The Hundredth Anniversary Meeting of the Society was held on 3rd April, 1941. The Council look forward to the time when fitting celebrations of the Society's Centenary will be possible, and are glad to report that Professor T. S. Moore has accepted the task of completing the Centenary History of the Society, begun by the late Professor J. C. Philip.

As a result of the Scheme of Co-operation between the Chemical Society, the Institute of Chemistry, and the Society of Chemical Industry, our Society entered upon its hundred-and-first year with a large increase in membership. In the list of nearly a thousand new Fellows are many names well known and honoured in the field of applied chemistry, and this gives encouragement to the hope that, in the years of development that lie ahead, the activities of the Chemical Society will have the direct support of a very high proportion of British chemists.

During 1941 the Chemical Council formulated a plan, which was accepted by the Councils of the participating bodies, for the establishment of a joint accounts office to which subscriptions would be

paid, and from which circular letters and publications would be distributed to members of the two publishing societies. This plan, a logical outcome of the joint subscription arrangements, should effect considerable economies by eliminating the overlap in the functions common to the two publishing societies, and it is expected that it will be possible to put the plan into operation during 1942.

I. FELLOWSHIP.

(1) *Fellowship Statistics.*

The number of Fellows on the 31st December, 1940, was 3695. During 1941, 863 Fellows were elected and 122 reinstated, the corresponding figures in 1940 being 153 and 11, respectively. The Society has lost 38 Fellows through death, 69 by resignation, and 57 by removal for non-payment of annual subscription, making a total loss of 164, compared with 242 in 1940. The number of Fellows on the 31st December, 1941, therefore, was 4516; of these, 1335 are joint members of the three Bodies, and 364 joint two-Body members. Of the joint members of the three Bodies, 585 were Fellows of the Chemical Society in 1940 and 750 are new Fellows; of the joint two-Body members, the corresponding figures are 293 and 71.

The names of those Fellows to whom the Council have conveyed the congratulations of the Society on completing 60 and 50 years of Fellowship have appeared in the *Proceedings*.

(2) *Deaths.*

The Council record with sorrow the death on 6th August of Professor J. C. Philip, who was elected President on 3rd April, and they deplore the deaths of three of their distinguished Honorary Fellows, Professor Herbert Freundlich, Professor Walther Nernst, and Professor Paul Sabatier.

The Council have arranged for obituary notices of Professor J. C. Philip and Professor Freundlich to be published in the *Journal*, but have had to postpone for the present the question of paying a tribute to the memory of Professor Nernst and of Professor Sabatier.

The Council also record with regret the death of Mr. W. B. Keen, of Messrs. W. B. Keen & Co., who have acted as Auditors to the Society since 1903.

(3) *Honours.*

The congratulations of the Society have been conveyed to Sir Shanti S. Bhatnagar, on his receiving the honour of Knighthood, to Mr. E. M. Rich, on his being made a C.B.E., and to Mr. R. Murdin Drake, Commander C. F. Goodeve, R.N.V.R., and Mr. E. R. Thomas on receiving the O.B.E.

The Council record with pleasure that the Davy Medal of the Royal Society for 1941 has been awarded to Dr. H. D. Dakin, and that the first award of the Paracelsus Gold Medal has been made to Sir Robert Robinson by the Swiss Chemical Society.

II. PUBLICATIONS.

(1) *Journal.*

During the year 210 papers were received by the Society; of these 3 were declined.

In addition to Obituary Notices and reports on Atomic Weights and the Annual General Meeting, the *Journal* for 1941, occupying 878 pages, contains 155 memoirs (26 on General, Physical, and Inorganic Chemistry, and 129 on Organic Chemistry), 15 notes, and 4 lectures, including the Presidential Address. The corresponding figures for 1940 are 1576 pages, 297 memoirs, 15 notes, and 5 lectures.

(2) *Abstracts.*

The report of the Bureau of Chemical and Physiological Abstracts for 1940 appears as Appendix A to this report.

(3) *Annual Reports.*

Volume XXXVII (1940) of the *Annual Reports on the Progress of Chemistry*, published in June 1941, contained 477 pages.

III. MEETINGS.

(1) *Scientific Meetings.*

During the year, 7 lectures have been held in London and 26 meetings outside London. A complete list of these is given in Appendix C.

(2) *Annual General Meeting.*

The Anniversary Meetings of the Society were held in London on 3rd April, 1941, and a full report appeared in the *Journal* for April.

IV. LIBRARY.

The Report of the Joint Library Committee for 1941 is given in Appendix B.

V. THE CHEMICAL COUNCIL.

The agreement between the three Chartered Chemical Bodies and the Chemical Council has been extended for seven years as from the 1st July, 1940.

VI. ADVISORY RESEARCH COUNCIL OF THE CHEMICAL SOCIETY.

The Advisory Research Council of the Chemical Society has continued to receive offers of assistance from Supervisors of Research, and has now allocated 215 topics of research. The War Cabinet Scientific Advisory Committee, through Lord Hankey the Chairman, has expressed appreciation of its work.

The Scheme initiated last year to meet, through the agency of volunteer workers, demands for fine chemicals required for work of national importance and not available through normal channels has continued to function with success. The Advisory Research Council received with regret the resignation of Dr. D. H. Hey as Chairman of the Fine Chemicals Sub-Committee and expressed its appreciation of his valuable services. Dr. J. C. Smith was appointed to this Office.

VII. ADMINISTRATION.

(1) *Presidency.*

In September, Dr. W. H. Mills was appointed President until the next Annuel General Meeting.

(2) *Elected Ordinary Members of Council.*

Dr. D. H. Hey retired from the Council on leaving the London area in December. The vacancy has not been filled.

(3) *Local Representatives.*

The resignations of Dr. G. N. Burkhardt and Dr. E. A Moelwyn-Hughes as Local Representatives for Manchester and Cambridge, respectively, were received with regret, and the Council expressed their appreciation of their services. Dr. A. E. Gillam and Dr. F. S. Dainton were appointed to fill the vacancies. Dr. A. McGookin, whose term of office has expired, has consented to serve for a further period.

VIII. FINANCE.

(1) *Contributions.*

The Council have received £1050 from the Chemical Council; the Royal Society has contributed £400 from the Rockefeller Grant in aid of Scientific Publications and £300 from the Government Publications Grant. The Council have expressed their sincere thanks for these substantial sums, and have acknowledged with gratitude contributions to the Publications Fund received from the following Fellows: Messrs. P. Appleyard, N. Campbell, P. K. Dutt, T. Ewan, W. E. Garner, F. A. Freeth, J. C. Jennings, F. W. Kirkbride, J. Bruce Miller, D. H. Peacock, W. G. Polack, J. E. B. Price, Sir David Rivett, H. G. Rule, F. C. Smith, E. E. Tallis, R. B. Turbutt, G. Watson Young.

Gifts of the Society's publications have been received from the following, to whom the Council have expressed their thanks: Messrs. A. F. Campbell, G. V. Davies, E. R. Marle, Miss C. M. G. Mohrhenn, R. Raper, C. H. Wright, and G. H. Wyatt. Contributions to the Library have been received with gratitude from Mr. J. E. B. Price, Sir Prafulla C. Rây, and Mr. J. C. Somerville, and the Society's collection of Medals has been enriched by the Nobel Gold Medal received under the Will of the late Sir Arthur Harden.

(2) *Bequests.*

A bequest of £1000 for the Publications Fund has been received from the late Mr. Robert Henry Parker, and further sums of £101 11*s.* 5*d.*, and £43 17*s.* 1*d.* from the Gilles and Tilden Bequests, respectively.

(3) *Travelling Expenses of Members of Council.*

In May, the Council decided that Members of Council living more than 50 miles from London should be entitled to claim an amount not exceeding the third-class return fare from their place of residence to the place of the Council Meeting. Members of Council are also entitled to make an additional claim up to an amount not exceeding the difference between the third- and first-class fares if they are unable to complete the double journey in one day.

(4) *War Damage Insurance.*

Though insurance against war damage is not compulsory in the case of a Society recognised as a Charitable Institution such as the Chemical Society, the Council has insured the property of the Society for £37,500.

IX. REPRESENTATION ON JOINT COMMITTEES AND ON OTHER BODIES.

The Society's representatives are as follows:

Bureau of Chemical and Physiological Abstracts:
Dr. H. J. T. Ellingham, Professor C. R. Harington, Dr. G. A. R. Kon, and Dr. C. W. Davies (Honorary Secretary), with the Treasurer ex-officio.

Chemical Council:
Dr. C. W. Davies, Mr. F. P. Dunn, Dr. L. H. Lampitt.

Joint Library Committee:
Professor A. J. Allmand, Professor H. Bassett, Dr. O. L. Brady, Professor C. H. Desch, Mr. M. B. Donald, Dr. H. J. T. Ellingham, Dr. H. J. Emeléus, Dr. C. F. Goodeve, Dr. P. Haas, Professor C. R. Harington, Dr. T. A. Henry, Dr. E. W. McClelland, Dr. E. E. Turner, and Professor W. Wardlaw.

Bristol University Court:
Professor F. G. Donnan.

British National Committee for Chemistry:
Dr. C. W. Davies (Honorary Secretary), Professor F. G. Donnan, and Mr. F. P. Dunn (Treasurer).

British Standards Institution:
Council of Chemical Division: Dr. J. J. Fox.
Technical Committees:
Co-ordinating the work of the Divisional Councils in regard to any British Standard which may be issued in future for units, conversion factors, fundamental formulæ, values for properties or materials, etc.: Dr. H. J. T. Ellingham.
Specifications for Materials and Plant used in Electroplating: Dr. U. R. Evans.
Standardisation of Scientific Glassware: Mr. F. R. Ennos.
Standards for use in Dairying Chemistry: Mr. Eric Voelcker.
Standardisation of Letter Symbols: Dr. C. F. Goodeve.

City and Guilds of London Institute:
The President.

Faraday Society:
Colloid Committee: Mr. D. C. Henry.

Lawes Agricultural Trust:
Committee of Management: Dr. E. F. Armstrong.

Royal Society:
Joint Standing Committee for Symbols and Abbreviations: Dr. C. W. Davies and Dr. H. J. T. Ellingham.

X. ACKNOWLEDGMENTS.

The Council are glad of this opportunity of expressing their gratitude to those Fellows who have continued to give their services freely to the Society during the year. They would especially mention Local Representatives, referees of papers for the *Journal*, contributors to the *Annual Reports*, and those delivering lectures.

APPENDIX A.

REPORT OF THE BUREAU OF CHEMICAL AND PHYSIOLOGICAL ABSTRACTS FOR 1941.

The Bureau, in common with other scientific publishing organisations, has had a number of difficulties with which to contend during the past year, not least in importance being the impossibility of obtaining certain foreign journals.

Attempts have been made by the Bureau to stimulate official interest in this matter, but without success. The Committee, however, is concerned at the natural repercussions of this lack of journals: journals which will arrive after the war and the abstracting of which will then throw considerable strain on the finances of the Bureau. In this connexion it is of interest to recollect that the Bureau is unique

in its constitution, particularly from the financial aspect. The responsibility for the finance of A I and A II lies with the Chemical Society, of B I, B II, and B III with the Society of Chemical Industry, and of A III with the Bureau itself. The original sponsor societies (the Chemical Society and the Society of Chemical Industry) have already put sums of money aside for post-war publications; the Bureau proposes to do the same for A III.

The appointment of an Honorary Treasurer last year has considerably simplified the consideration of the finances of the Bureau, and in pursuance of this thought the Committee are of opinion that the more autonomous the Bureau becomes, the more efficiently will its duties be carried out.

For a number of years, figures of the Annual Income and Expenditure Account of the Bureau have been published, but as these have shown certain items only of the expenditure on abstracts (they have not included cost of printing and paper, overheads, etc.) the Committee, on the advice of the Honorary Treasurer, has decided to cease publication of these figures, which can only be misleading to those who read them without a full knowledge of their limitations.

It is obviously desirable that the Bureau should publish figures which will enable the scientific fraternity to realise the cost of this work, and it is hoped that in the near future the consent of the sponsoring societies will be obtained to such a procedure.

Other items of interest arising out of the work of the Bureau for the past year have been: (1) the economies effected, particularly in respect of saving of paper, by the adoption of the smaller type; (2) the difficulties of publishing the Abstracts on the first of each month owing to shortage of staff at the printers and other difficulties inherent in present conditions; these the Bureau is endeavouring to overcome; (3) the publication of the whole of the Quinquennial Index; (4) the rearrangement of Abstracts A II.

During the year the Bureau held seven meetings and the Finance Committee six.

Finance.

The Finance Committee has continued to present to the Bureau detailed statements showing the whole of the costs of producing the abstracts in the various sections for each quarter of the year, and is now presenting quarterly statements to the Chemical Society and the Society of Chemical Industry of the funds required to meet estimated expenditure for the succeeding quarter.

The methods of allocating among the various sections costs of certain items of expenditure and overheads have been modified.

Abstracts.

Starting with the issues of January, 1941, the classes of abstracts in A II and in the three sections of B were re-numbered to give the number I to the first class in each of these four sections, thus bringing them in line in this respect with Abstracts A I and A III.

Statistics.—The figures given in the appended table show the number of abstracts and pages printed in each section during 1941, together with comparative figures for 1940.

	A I.				A II.			
	1940.		1941.		1940.		1941.	
	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	1471	136	683	46	606	112	308	40
2nd ,, ...	1525	138	1016	70	734	130	381	50
3rd ,, ...	1200	106	858	62	444	78	403	48
4th ,, ...	747	68	955	68	335	66	459	56
	4943	448	3512	246	2119	386	1551	194

	A III.			
	1940.		1941.	
	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	3225	276	2065	118
2nd ,, ...	3442	274	1893	124
3rd ,, ...	2858	230	1908	116
4th ,, ...	2169	166	3100	186
	11,694	946	8966	544

B.

	1940.		1941.	
	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	2798	250	2493	152
2nd ,, ...	2719	252	2401	160
3rd ,, ...	2380	208	2820	182
4th ,, ...	2126	194	2964	190
	10,023	904	10,678	684

	1941.					
	B I.		B II.		B III.	
	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	1010	58	775	52	708	42
2nd ,, ...	986	66	706	52	709	42
3rd ,, ...	1387	84	841	58	592	40
4th ,, ...	1262	74	934	64	768	52
	4645	282	3256	226	2777	176

It will be seen that all the sections of A abstracts show a considerable decrease, amounting to some 20—25%, compared with 1940. Abstracts B, on the other hand, show an increase of about 6%, due to certain arrears in sundry journals and patents having been cleared off.

Abstracts A II.—A Sub-Committee was appointed by the Bureau to report on criticisms which had been received regarding faulty classification of certain abstracts in Section A II. The Sub-Committee recommended a revised classification of the abstracts in this Section, involving the addition of three new sub-sections, the revision of the name of another, and the inclusion of all abstracts on organo-metallic compounds in one class, as well as the transfer of the "Miscellaneous" section to follow "Proteins." Further recommendations were that an extended system of cross-references within each section be introduced and that every abstract should commence with a concise statement of the scope of the paper unless this was clearly indicated in the title.

These recommendations, approved by the Chemical Society, were adopted by the Bureau, with the addition that the system of cross-references should also apply to A I. They will be put into effect in the beginning of 1942.

The Bureau also endorsed the opinion expressed by the Sub-Committee that the value of the Abstracts would be much enhanced by the inclusion of a formula index as soon as circumstances permit.

Abstracts A III.—The Bureau is gratified to record that the Anatomical Society of Great Britain and Ireland has decided to continue its annual contribution to the A III fund at least until the end of 1942, and has expressed the hope that financial considerations will permit it to support the fund after that date. The Society has, moreover, expressed its appreciation of the work being done by the Bureau in publishing abstracts of anatomical papers. The Society of Chemical Industry has made a grant of £50 towards the expenses of A III, and the Bureau is encouraged in its work by the Society's action in once again showing its appreciation of Abstracts A III.

A highly gratifying mark of the sympathy of organisations outside the Bureau was the receipt, from the Royal Society, of a grant of £250 from the American Physiological Society's gift. This grant has been transferred by the Bureau to the A III fund.

It will be seen from the Income and Expenditure Account that the gross receipts from sales of Abstracts during 1941 have been maintained at almost the same level as in 1940, despite a decreased number of subscribers; the increase in the published price of this section has been fully justified. Partly as a result of a reduction of about 20% in the volume of abstracts printed, and partly owing to the increased grants so generously made to the fund by the supporting Societies, the income of the fund has exceeded the expenditure for the first time. £700 has been transferred to a Reserve Fund.

On the Editorial side of A III, Dr. E. Boyland has handed over the sub-editing of abstracts on "Tumours" to Dr. A. Haddow, and Dr. E. A. Carmichael is no longer able to assist Professor Wright with the section on the "Nervous System."

Abstracts B.—Despite the increase in the number of abstracts printed and the increases in costs of printing and paper, the total cost of printing Abstracts B, including paper, was approximately the same in 1941 as in 1940. This is partly due to the change in type and partly to the sub-division of B Abstracts into three sections, which has resulted in a smaller number of copies being required. A very substantial saving in the amount of paper used has been achieved.

BUREAU OF CHEMICAL AND PHYSIOLOGICAL ABSTRACTS.

INCOME AND EXPENDITURE ACCOUNT OF ABSTRACTS A III FOR THE YEAR ENDED 31ST DECEMBER, 941.

1940 £ s. d.	1940 £ s. d.	*Income.*	1941 £ s. d.	1941 £ s. d.
	2050 8 5	To Sales of Abstracts A III		2252 17 4
	10 6	„ Sales of Physiological Abstracts		
		„ Contributions :		
1300 0 0		The Chemical Society (Annual Grant) ...	1500 0 0	
200 0 0		„ „ „ (Additional Grant) ...		
300 0 0		The Physiological Society	400 0 0	
200 0 0		The Biochemical Society	300 0 0	
100 0 0		The Anatomical Society	100 0 0	
50 0 0		The Society of Chemical Industry	50 0 0	
		The Royal Society (Grant from American Physiological Society's gift)	250 0 0	
	2150 0 0			2600 0 0
	2 5 6	„ Interest on Deposit		2 10 8
49 10 9		„ Proceeds of Advertisements	56 8 0	
14 0 0		*Less* Commission	12 0 0	
	35 10 9			44 8 0
	189 12 9	„ Excess of Expenditure over Income carried to Balance Sheet		
	£4428 7 11			£4899 16 0

1940 £ s. d.	1940 £ s. d.	*Expenditure.*	1941 £ s. d.	1941 £ s. d.
	510 5 9	By Editorial Salaries		569 0 6
	25 9 5	„ „ Postages		34 2 7
	927 8 10	„ Abstractors' Fees		729 12 3
	1607 4 2	„ Printing and Paper		1359 15 10
	30 1 6	„ Banding		27 1 11
	181 13 1	„ Distribution		94 5 2
	100 9 1	„ Miscellaneous		35 16 8
		„ Index :	£ s. d.	
235 16 3		Editorial Salaries	238 1 7	
11 2 7		Superannuation	11 11 6	
482 1 2		Printing and Paper	454 0 4	
10 19 7		Banding	2 15 2	
34 16 1		Distribution	30 14 7	
33 15 7		Miscellaneous	22 14 11	
	808 11 3			759 18 1
	160 4 5	„ Overhead Expenses (Proportion) Chemical Society		151 3 4
	77 0 5	„ Overhead Expenses (Proportion) Society of Chemical Industry		47 9 11
		„ War Damage Insurance		2 6 10
	4428 7 11			3810 13 1
		„ Transfer to Reserve Fund for Abstracts in Suspense		700 0 0
		„ Excess of Income over Expenditure, carried to Balance Sheet		389 2 11
	£4428 7 11			£4899 16 0

BALANCE SHEET OF ABSTRACTS A III FOR THE YEAR ENDED 31ST DECEMBER, 1941.

Liabilities. £ s. d.	£ s. d.	£ s. d.	*Assets.* £ s. d.	£ s. d.	£ s. d.
1249 7 0	To Sundry Creditors	1863 4 2		185 13 11	By Sundry Debtors	385 12 10
	„ Excess of Income over Expenditure for year	389 2 11		675 3 8	„ Cash at Bank	1478 4 10
	Less Excess of Expenditure over Income brought forward	388 9 5	189 12 9		„ Excess of Expenditure over Income for year	— — —
		13 6	198 16 8		*Add* Excess of Expenditure over Income brought forward	— — —
				388 9 5		
		£1863 17 8		£1249 7 0		£1863 17 8

BALANCE SHEET OF ABSTRACTS A III RESERVE FUND FOR THE YEAR ENDED 31ST DECEMBER, 1941.

Liabilities. £ s. d.	£ s. d.	*Assets.* £ s. d.	£ s. d.
— — —	To Cash Receivable...	700 0 0	— — — By Sundry Debtor...	700 0 0

F. P. DUNN, *Treasurer of Bureau.*

We have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers, and certify them to be in accordance therewith. We have also verified the Balances at the Bankers. Certain figures have not yet been subjected to audit by the Auditors of the Bureau and are therefore liable to adjustment.

W. B. KEEN & CO.,
Chartered Accountants.

224, REGENT STREET, W.1.
27th February, 1942.

At the suggestion of the Council of the Society of Chemical Industry, a notice has been inserted in the Abstracts inviting readers to apply to the Editor for information as to where the various journals abstracted may be consulted.

Collective Indexes.

The demands for copies of the Decennial Index 1923—1932 continues, and the Bureau has refunded one half of the balance of £100 from recent sales to the Chemical Society and the same amount to the Society of Chemical Industry.

Both volumes of the Quinquennial Index 1932—1937 were published during the year, the Name Index (1964 pp.) in January and the Subject Index (1584 pp.) in November. The Bureau feels that it was no small achievement to issue the complete Index in less than a year, under the circumstances, and welcomes this opportunity of recording its high appreciation of the efforts of the Indexer and her staff and of the Printers in producing such excellent volumes.

The Chemical Society and the Society of Chemical Industry have agreed to the proposal of the Bureau to proceed with the preparation of a Collective Index covering the period 1938—1942, and work on this Index is now in progress.

General.

Offices.—After an absence of about a year at South Kensington, the Bureau returned to Clifton House in the Autumn and has accorded its sincere thanks to Governing Body of the Imperial College for having granted it accommodation in the Royal Sch of Mines.

Staff.—There have been several changes among the staff of the Office and Indexing Department during the year. Miss Tanner, the Assistant Indexer, has resigned, and arrangements have been made for distributing her work among the remaining staff as a temporary measure.

QUINQUENNIAL INDEX ACCOUNT TO END OF JANUARY, 1941.

(Subject to audit.)

	£	s.	d.		£	s.	d.
Balance forward from 1940	810	7	2	Salaries	285	8	8
Receipts less refunds	1117	7	5	Rent	26	5	0
Grants	2250	0	0	Printing Names Volume	1940	5	6
Bank interest	1	12	9	,, Subjects Volume	1640	3	9
				Postage on volumes	63	4	1
				Sundry expenses	52	5	10
				Balance	171	14	6
	£4179	7	4		£4179	7	4

APPENDIX B.

REPORT OF THE JOINT LIBRARY COMMITTEE, 1941.

During the year there were 3836 attendances, as compared with 4381 in 1940. Of these 3658 were made by the three Constituent Bodies (the Chemical Society, Institute of Chemistry, and Society of Chemical Industry) or by persons introduced by them, and 178 by other Contributing Bodies, as against 4160 and 221 in 1940.

The number of books borrowed was 4858, against 4307 in the previous year; of these 2143 were issued by post, compared with 1702 in the preceding year.

The Library telephone calls included 881 enquiries which necessitated reference to books in the Library, as against 741 the previous year.

950 pages of printed matter were photocopied, as against 1159 the preceding year.

The additions to the Library comprise:

90 books, of which 26 were presented, 347 volumes of periodicals and 163 pamphlets, as against 115 books, 432 volumes of periodicals, and 202 pamphlets, last year.

The total number of volumes added during the year was 437. The Library now contains 44,630 volumes, consisting of 13,257 books and 31,373 bound volumes of periodicals.

Analysis.

	Attendances.	Books borrowed.	Books added.	Volumes of periodicals.	Pamphlets.
1941	3836	4858 (2142 by post)	90	347	163
1940	4381	4307 (1702 by post)	115	432	202

The fewer attendances are mainly due to the fact that in consequence of enemy action it was necessary to close the Library for reference purposes from 17th April to 10th May, inclusive. It was, however, possible to lend books to callers and by post, and this in part accounts for the considerable increase in books borrowed.

No books were damaged as a direct result of enemy action, but a few volumes were damaged during subsequent repairs to the roof.

A considerable number of duplicate serials have been removed to places of greater safety, and, as in previous years, these removals have provided temporary space for current additions. The necessity for providing adequate Library accommodation, a subject which has now been under consideration for over 40 years (see Presidential Address, *J.C.S.*, 1901, **79**, 880), is still a vital one, and a most acute problem will occur at the close of hostilities, when the question will arise of the return of volumes removed for safety, for which it will not be possible to find room in the present building.

The Committee wishes to record its grateful appreciation of the gifts received from Fellows and others during the year, and its thanks to the Librarian and staff, who, in spite of current difficulties, have maintained the service of the Library at almost peace-time level.

APPENDIX C.

LECTURES AND DISCUSSIONS.

3rd April. *Presidential Address* on "The Mechanism of the Benzidine Re-arrangement and some Related Topics," by Sir Robert Robinson.

Lectures given in London.

24th April. *Tilden Lecture* on "Some Themes in the Chemistry of Macromolecules," by Professor H. W. Melville; 15th May, *Eighth Liversidge Lecture* on "Complex Formation," by Professor N. V. Sidgwick; 19th June, *Tilden Lecture* on "Vitamins of the B Group," by Professor A. R. Todd; 16th October, *Eighth Hugo Miller Lecture* on "Some Aspects of Algal Chemistry," by Professor I. M. Heilbron; 30th October (Joint Meeting with the Plastic Group of the Society of Chemical Industry), on "The Constitution of Plastics," by Dr. C. Redfarn; 20th November, on "X-Rays and the Stoichiochemistry of the Proteins," by Dr. W. T. Astbury.

Lectures given outside London.

Bristol. At the University: 5th June, on "Liquid Crystals," by Professor G. M. Bennett.

Edinburgh. At the North British Station Hotel (joint meeting with the Institute of Chemistry and the Society of Chemical Industry): 27th January, on "Nucleic Acids," by Professor J. M. Gulland; 24th February, at the North British Station Hotel, *Tilden Lecture* on "Some Problems in Macromolecular Chemistry," by Professor H. W. Melville; 11th November, at the University (joint meeting with the Edinburgh University, the Chemical Society, and the local sections of the Institute of Chemistry and Society of Chemical Industry), on "The Crystallisation of Graphite," by Professor H. L. Riley.

Glasgow. At the Royal Technical College: 21st February, on "Correlations between Cancer-producing Compounds," by Professor J. W. Cook; 7th November, on "Forty Years of Optical Activity," by Professor T. S. Patterson.

Leeds. At the University (joint meeting with the University of Leeds Chemical Society): 11th March, Discussion on "Some Aspects of Adsorption," opened by Dr. R. M. Barrer and Mr. R. S. Bradley; 13th May, at the University, *Eighth Liversidge Lecture* on "Complex Formation," by Professor N. V. Sidgwick; 13th October, on "Analysis of Molecular Structure by X-Ray Methods," by Dr. J. Monteath Robertson.

Liverpool. At the University (joint meeting with the Liverpool University Chemical Society): 13th February, on "Some Chemical Aspects of Modern Bacteriological Research," by Professor H. D. Wright; 1st May, on "Chemical Research in Electrical Industry," by Dr. J. Brisley; 13th November, on "Some Recent Developments in the Experimental Study of Animal Fats," by Professor T. P. Hilditch.

Manchester. At the University (joint meeting with the Institute of Chemistry and Society of Chemical Industry): 8th November, on "Long Molecules," by Dr. H. Hunter and Mr. D. F. Howitt.

North Wales. At University College, Bangor: 7th November, on "Hemp Drugs," by Professor A. R. Todd.

Nottingham. At University College: 15th November, Eighth Hugo Müller Lecture on "Some Aspects of Algal Chemistry," by Professor I. M. Heilbron.

Oxford. In the Biochemistry Department, University Museum: 30th May, *Seventh Pedler Lecture* on "Recent Developments in the Chemistry of the Carbohydrates," by Professor W. N. Haworth.

St. Andrews and Dundee. At University College, Dundee: 24th January, on "The Teaching of Chemistry in the University of St. Andrews," by Sir James Irvine; 12th November, on "The Crystallisation of Graphite," by Professor H. L. Riley.

Sheffield. At the University: 28th February, on "Diazotisation," by Professor J. Kenner; 21st November (joint meeting with the Sheffield University Chemical Society): on "Polymers," by Professor H. W. Melville.

South Wales.

Cardiff. At University College of South Wales: 15th February, on "Disinfectants," by Mr. N. Berry, and on 21st March (both joint meetings with the Institute of Chemistry and Society of Chemical Industry): on "More Recent Investigations on Organic Compounds of Gold," by Professor C. S. Gibson; 18th April, on "Some Recent Developments in Microchemistry," by Dr. Janet W. Matthews; 1st November, on "Chemical Determination of Vitamins," by Dr. M. Pyke.

Swansea. At the Royal Institution, Swansea: 18th January (joint meeting with the local section of the Institute of Petroleum): on "The Combustion of Gaseous Hydrocarbons," by Mr. A. R. Ubbelohde; at University College (joint meeting with the University College of Swansea Students Chemical Society): 20th March, on "The Life and Work of William Jackson Pope," by Professor C. S. Gibson.

INCOME AND EXPENDITURE GENERAL PURPOSES ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1941.

Income.

1940 £ s. d.	1940 £ s. d.		1941 £ s. d.	1941 £ s. d.
	60 0 0	To Life Composition Fees (£66), one-third as Income		22 0 0
		Annual Subscriptions:		
		Single-body Fellows—		
668 16 8		Received in advance, on account of 1941	491 1 1	
7522 4 11		" during 1941 " " "	4683 17 10	
308 12 8		" " " " " 1940	249 1 4	
		" " " " " 1939 and previous years	9 0 0	
3 12 2		Joint two-body Fellows— Received on account of 1941	1026 0 10	
— — —		Joint three-body Fellows— Received on account of 1941	2632 1 6	
— — —			9091 2 7	
8503 6 5				
		Less Amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	270 0 0	
270 0 0			8821 2 7	
8233 6 5				
		Add Arrears at date: £1795 13*s.* 6*d.* Estimated to realise as per Balance Sheet	250 0 0	
270 0 0				9071 2 7
	8503 6 5			558 2 7
	625 18 5	" Dividends on Investments		396 1 0
	351 3 9	" Income Tax recovered		3 11 3
	3 11 2	" Interest on Deposit		2 0 0
	5 0 0	" Donations		56 8 2
	45 11 6	" Miscellaneous Receipts		
	463 10 11	" Balance, being Excess of Expenditure over Income carried to Balance Sheet		187 19 11
	£10,058 2 2			£10,297 5 6

Expenditure.

1940 £ s. d.	1940 £ s. d.		1941 £ s. d.	1941 £ s. d.
		By Administration Expenses:		
2415 8 2		Office Salaries and Wages	2533 0 9	
259 13 0		Superannuation	271 7 5	
314 8 11		House Expenses, etc.	331 16 5	
84 0 0		Accountants' Charges	84 0 0	
291 1 0		Miscellaneous Printing and Stationery	265 7 3	
191 17 6		Postages	199 19 10	
53 11 4		Miscellaneous	46 3 11	
3609 19 11			3731 15 7	
		Less Transfer to Publications and Library:		
333 3 0		Journal	£ 361 12 4	
276 17 3		Abstracts A I, A II	302 6 7	
160 4 5		" A III	151 3 4	
163 19 11		Library Account	159 6 10	
			974 9 1	2757 6 6
	2675 15 4			46 12 4
	35 19 5	" Expenses of Meetings		5 5 0
	5 5 0	" Donation		5269 9 6
	6055 8 6	" Contribution to Publications Fund		
		" Contribution to Library Fund:		
		For Fittings, Furniture, Books, Periodicals, and Binding	508 12 6	
340 15 1		For Air Raid Precautions	71 4 9	
68 3 8		For War Damage Insurance	579 17 6	
327 11 11		Proportion of Maintenance	330 8 9	
736 10 8			1490 3 6	
16 7 7		*Less* Balance from Library Account	88 8 3	
		Add Balance due to Library Account		1578 11 9
	720 3 1			137 7 8
	38 17 10	" Transfer to Staff Pensions Fund		
	200 0 0	" Transfer to Centenary Fund		86 11 9
	66 16 0	" Expenses of Local Representatives		6 16 6
	3 3 0	" Legal Expenses		1 3 3
	4 18 8	" Interest on Loans from other Funds		302 8 6
	251 15 4	" Air Raid Precautions		64 16 6
	— — —	" Travelling Expenses of Members of Council		
	— — —	" War Damage Insurance	699 17 6	
		Less Transfer to Publications and Library:	£ s. d.	
		Journal	31 8 1	
		Abstracts A I, A II	38 8 10	
		Abstracts A III	2 6 10	
		Library Account	579 17 6	
			652 1 3	
				47 16 3
	£10,058 2 2			£10,297 5 6

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1941.

PUBLICATIONS FUND.

1940 £ s. d.	1940 £ s. d.	*Income.*	1941 £ s. d.	1941 £ s. d.
		To Publication Sales (including back numbers):		
2768 6 2		Journals and Proceedings	2704 14 4	
1894 8 9		Abstracts, A I, A II	2123 1 8	
10 13 3		Collective Index, Vols. I–VI	8 5 0	
871 14 10		Annual Reports on Progress of Chemistry ...	618 7 3	
253 13 0		Authors' Extra Reprints	126 1 4	
5 15 6		Other Publications	2 6 0	
	5804 11 6			5582 15 7
		„ Proceeds of Advertisements:	£ s. d.	
442 16 1		Journal	532 15 5	
58 9 6		Annual Reports	72 10 0	
501 5 7			605 5 5	
143 15 2		*Less* Commission	178 8 5	
	357 10 5			426 17 0
49 10 9		A I, A II	56 8 0	
14 0 0		*Less* Commission	12 0 0	
	35 10 9			44 8 0
				471 5 0
		„ Donations:		
11 2 0		Fellows	13 2 6	
1000 0 0		Chemical Council	1000 0 0	
150 0 0		„ „ for Summaries to Papers in Journal	50 0 0	
	1161 3 0			1063 2 6
	550 0 0	„ Government Publications Grant (through the Royal Society)		300 0 0
	— — —	„ Allocation from the Rockefeller Grant (through the Royal Society)		400 0 0
	— — —	„ Transfer from Tilden Lecture Fund		25 4 0
	247 0 6	„ Dividends on Investments		223 18 9
	145 15 8	„ Income Tax recovered		182 11 4
	6055 8 6	„ Transfer from General Purposes Account (the balance of expenditure on publications) ...		5262 9 6
	£14,357 0 4			£13,511 6 8

1940 £ s. d.	1940 £ s. d.	*Expenditure.*	1941 £ s. d.	1941 £ s. d.
		By Expenses on account of Journal:		
1159 11 9		Editorial Salaries	1156 5 3	
85 12 6		Superannuation	85 12 6	
24 5 7		Editorial Postages	19 12 7	
3098 14 2		Printing and Paper	2502 11 2	
54 5 8		Banding	66 19 3	
552 12 0		Distribution	401 15 8	
516 15 6		Authors' Reprints	337 0 11	
14 3 2		Miscellaneous	10 7 9	
333 3 0		Overhead Expenses (proportion)	361 12 4	
— — —		War Damage Insurance	31 8 1	
	5839 3 4			4973 5 6
		„ Expenses on account of Abstracts A I, A II:		
732 9 2		Editorial Salaries	687 8 7	
29 7 1		Editorial Postages	54 0 7	
817 8 11		Abstractors' Fees	577 11 7	
1674 15 6		Printing and Paper	1384 15 2	
52 0 0		Banding	54 3 8	
225 14 6		Distribution	188 10 3	
98 5 10		Miscellaneous	44 1 4	
		„ Index:	£ s. d.	
208 7 0		Editorial Salaries	194 6 8	
9 16 3		Superannuation	9 7 4	
490 1 8		Printing and Paper	386 9 10	
13 11 8		Banding	3 11 2	
43 1 3		Distribution	39 12 11	
29 17 0		Miscellaneous	36 0 10	
				669 8 9
276 17 3		Overhead Expenses (proportion) Chemical Society	302 6 7	
65 9 6		Overhead Expenses (proportion) Society Chemical Industry	94 19 11	
		War Damage Insurance	38 8 10	
	4767 2 7			4095 15 3
1300 0 0		„ Agreed contribution to Abstracts A III ...	1500 0 0	
200 0 0		„ Additional contribution to Abstracts A III ...	— — —	
	1500 0 0			1500 0 0
	1100 0 0	„ Transfer to Special Reserve Fund for publications		1800 0 0
	300 0 0	„ Transfer for Quinquennial Index, 1933–1937		100 0 0
	850 14 5	„ Annual Reports on the Progress of Chemistry: Printing and Honoraria		1042 5 11
	£14,357 0 4			£13,511 6 8

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1941.

LIBRARY.

1940 £ s. d.	1940 £ s. d.	*Income.*	1941 £ s. d.	1941 £ s. d.
		To Contribution for Fittings, Furniture, Books, Periodicals and Binding:		
340 15 1		Transfer from General Purposes Account ...	508 12 6	
200 0 0		„ „ Herbert Spencer Bequest ...	— — —	
		„ Air Raid Precautions:		
68 3 8		Transfer from General Purposes Account ...	71 4 9	
		„ War Damage Insurance:		
— — —		Transfer from General Purposes Account ...	579 17 6	
	608 18 9			1159 14 9
		„ Contributions through the Chemical Council towards maintenance:		
327 11 11		Chemical Society (transfer from General Purposes Account)	330 8 9	
682 11 4		Institute of Chemistry	674 7 6	
354 19 5		Society of Chemical Industry	343 18 10	
250 0 0		The Chemical Council	250 0 0	
	1615 2 8			1598 15 1
		„ Contributions, etc., received from other sources towards maintenance:		
100 0 0		Association of British Chemical Manufacturers	100 0 0	
21 0 0		Biochemical Society	21 0 0	
26 5 0		Faraday Society	26 5 0	
50 0 0		Institute of Brewing	50 0 0	
10 10 0		Society of Dyers and Colourists	10 10 0	
21 0 0		Society of Public Analysts	21 0 0	
3 0 0		Fellows	6 3 0	
5 19 4		Miscellaneous receipts	8 1 7	
	237 14 4			242 19 7
		„ Balance, amount transferred from General Purposes Account		88 8 3
	£3461 15 9			£3089 17 8

1940 £ s. d.	1940 £ s. d.	*Expenditure.*	1941 £ s. d.	1941 £ s. d.
		By Capital and Extraordinary Expenditure:		
208 6 1		Books and Periodicals *	192 3 6	
132 9 0		Binding	66 9 0	
		Transfer to Special Reserve Fund for Books and Binding	250 0 0	
200 0 0		Air Raid Precautions	71 4 9	
68 3 8		War Damage Insurance	579 17 6	
— — —				
	608 18 9			1159 14 9
		„ Maintenance:		
1465 19 6		Salaries	1535 9 9	
181 1 0		Superannuation of Library Staff	184 6 6	
17 12 10		Postages	23 13 4	
7 16 2		Miscellaneous Expenses	27 6 6	
163 19 11		Overhead Expenses (proportion)	159 6 10	
	1836 9 5			1930 2 11
	16 7 7	„ Balance, amount transferred to General Purposes Account...		— — —
	£3461 15 9			£3089 17 8

* Other than those received in exchange.

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1941.

SPECIAL RESERVE FUND.

1940	*Income.*	1941	1940	*Expenditure.*	1941
£ s. d.		£ s. d.	£ s. d.		£ s. d.
— — —	To Dividends on Investments	23 18 4	— — —	By Balance, being Excess of Income over Expenditure carried to Balance Sheet	24 3 3
— — —	„ Interest on Deposit	4 11			
		£24 3 3	— — —		£24 3 3

RESEARCH FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
438 2 7	To Dividends on Investments	414 3 1	— — —	By Honorarium, Hugo Müller Lecture	21 0 0
224 4 11	„ Income Tax recovered	309 0 0	210 10 0	„ Grants	80 0 0
67 9 8	„ Repayment of Grants	48 13 7	5 10 0	„ Miscellaneous Expenses	2 17 8
4 0 0	„ Grants not applied for	— — —		„ Balance, being Excess of Income over Expenditure, carried to Balance	
5 11 10	„ Interest on Deposit	12 14 7	528 2 1	Sheet	680 13 7
3 11	„ Interest on Loan to General Purposes Account	— — —			
4 9 2	„ Sale of Apparatus				
		£784 11 3	£744 2 1		£784 11 3
£744 2 1					

SPECIAL PUBLICATIONS FUND.

£ s. d.	£ s. d.		£ s. d.	£ s. d.		£ s. d.
		To Sales of Publications:			By Honorarium, Centenary Volume	25 0 0
6 15 3		Memorial Lecture, Vol. I	5 15 0	— — —		— — —
5 2 0		„ „ Vol. II	4 15 9	3 11 6	„ Reprints for Memorial Lectures, Vol. IV	— — —
7 19 9		„ „ Vol. III	5 10 4	8 11 1	„ Reprints for Faraday Lectures, Vol. II	
3 2 6		Faraday Lectures	2 8 6		„ Balance, being Excess of Income over Expenditure carried to Balance	
1 8 10		Portraits	2 6	91 19 6	Sheet	73 7 10
1 1 9		Other publications	2 13 10			
	25 10 1			21 5 11		
	74 0 8	„ Dividend on Investments		74 0 8		
	3 19 11	„ Interest on Deposit		1 18 0		
	11 5	„ Interest on Loan to General Purposes Account ...		1 3 3		
	£104 2 1		£98 7 10	£104 2 1		£98 7 10

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1941.

SPECIAL LECTURES FUND.

1940	*Income.*	1941	1940	*Expenditure.*	1941
£ s. d.		£ s. d.	£ s. d.		£ s. d.
35 13 0	To Dividends on Investments	34 15 8	— — —	By Honoraria	50 0 0
8 1 10	„ Income Tax recovered	9 16 6	— — —	„ Lecture Expenses	10 0
17 0	„ Interest on Deposit	9 4	44 11 10	„ Balance, being Excess of Income over Expenditure, carried to Balance Sheet	— — —
— — —	„ Balance, being Excess of Expenditure over Income, carried to Balance Sheet	5 8 6			
£44 11 10		£50 10 0	£44 11 10		£50 10 0

STAFF PENSIONS FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
88 17 10	To Transfer from General Purposes Account	137 7 8	80 0 0	By Pension paid during 1941	80 0 0
34 12 0	„ Dividends on Investments	34 14 4	— — —	„ Balance, being Excess of Income over Expenditure, carried to Balance Sheet	100 0 0
6 10 2	„ Income Tax recovered	7 18 0			
£80 0 0		£180 0 0	£80 0 0		£180 0 0

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
32 5 6	To Dividends on Investments	27 17 9	50 7 9	By Balance, being Excess of Income over Expenditure, carried to Balance Sheet	49 13 5
17 11 4	„ Income Tax recovered	21 6 9			
10 11	„ Interest on Deposit	8 11			
£50 7 9		£49 13 5	£50 7 9		£49 13 5

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1941.

CENTENARY FUND.

1940	Income.	1941	1940	Expenditure.	1941
£ s. d.		£ s. d.	£ s. d.		£ s. d.
200 0 0	To Contribution from General Purposes Account	— — —			
19 7 7	„ Interest on Deposit in Post Office Savings Bank and London Savings Bank	25 1 11	223 6 9	By Balance, being Excess of Income over Expenditure carried to Balance Sheet	25 1 11
3 19 2	„ Interest on Loan to General Purposes Account	— — —			
£223 6 9		£25 1 11	£223 6 9		£25 1 11

THE HERBERT SPENCER BEQUEST.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
17 10	To Interest on Deposit in Post Office Savings Bank and London Savings Bank	— — —	200 0 0	By Transfer to Library Account for purchase of Books	— — —
4 2	„ Interest on Loan to General Purposes Account		34 0 0	„ Purchase of Office Furniture	24 9 6
232 18 0	„ Balance, being Excess of Expenditure over Income carried to Balance Sheet	24 9 6			
£234 0 0		£24 9 6	£234 0 0		£24 9 6

THE FARADAY LECTURE FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
7 11 0	To Dividends on Investments	7 1 1			
4 11 10	„ Income Tax recovered	5 11 7	12 2 10	By Balance, being Excess of Income over Expenditure carried to Balance Sheet	12 12 8
£12 2 10		£12 12 8	£12 2 10		£12 12 8

THE TILDEN LECTURE FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
48 2 7	To Dividends on Investments	43 4 3	15 15 0	By Honoraria	31 10 0
20 6 9	„ Income Tax recovered	25 19 4	2 19 2	„ Lecture Expenses	10 6 2
7 6	„ Interest on Deposit	5 0	12 12 0	„ Transfer to Publications Fund, for cost of publication of Lectures	25 4 0
			37 10 8	„ Balance, being Excess of Income over Expenditure carried to Balance Sheet	2 8 5
£68 16 10		£69 8 7	£68 16 10		£69 8 7

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1941.

GENERAL PURPOSES.

1940 £ s. d.	1940 £ s. d.	*Liabilities.*	1941 £ s. d.	1941 £ s. d.
	538 1 1	To Subscriptions received in advance ...		220 9 11
	2,508 1 8	„ Sundry Creditors (Printing and other Expenses)		3,195 15 4
	900 0 0	Reserve for Quinquennial Index, 1933–1937	900 0 0	
		Add Transfer Publications Fund ...	100 0 0	
			1,000 0 0	
	— — —	*Less* Amount paid to Bureau of Chemical and Physiological Abstracts ...	1,000 0 0	— — —
		„ Loans from other Funds :		
600 0 0		Special Publications Fund	700 0 0	
700 0 0		Research Fund	— — —	
100 0 0		Special Lectures Fund	— — —	
500 0 0		„ Reserve Fund	2,050 0 0	
	1,900 0 0			2,750 0 0
	2,000 0 0	„ Loan, The Chemical Council		1,000 0 0
21,888 19 10		„ Excess of Assets over Liabilities as per last Balance Sheet	23,563 11 8	
100 0 0		*Add* Amount received from Executors of Emile Mond—Legacy	— — —	
120 0 0		*Add* Life Composition Fees (two-thirds)	44 0 0	
2,018 2 9		*Add* Interest on deposit with United Kingdom Provident Institution *re* Superannuation	148 15 0	
24,127 2 7			23,756 6 8	
463 10 11		*Deduct* Excess of Expenditure over Income for year	£ s. d. 187 19 11	
100 0 0		*Deduct* Amount transferred to Special Reserve Fund : Emile Mond Legacy	— — —	
— — —		*Deduct* Amount transferred to Staff Pensions Fund *re* Superannuation	2,166 17 9	
	23,563 11 8		2,354 17 8	21,401 9 0
	£31,409 14 5			£28,567 14 3

1940 £ s. d.	*Assets.*	1941 £ s. d.
25,931 8 0	By Investments as per Schedule (cost or value when acquired)	25,931 8 0
2,018 2 9	„ United Kingdom Provident Institution : Amount on Deposit	— — —
2,236 1 5	„ Sundry Debtors	1,736 3 4
270 0 0	„ Subscriptions in Arrear, £1,795 13*s.* 6*d.* Estimated to realise ...	250 0 0
688 7 1	„ Stock of Paper (Journal, and Annual Reports)	377 7 9
265 15 2	„ Cash in hand	272 15 2
£31,409 14 5		£28,567 14 3

THE CHEMICAL SOCIETY. BALANCE SHEETS, 31ST DECEMBER, 1941.

SPECIAL RESERVE FUND.

1940	*Liabilities.*	£ s. d.	1941 £ s. d.	1940	*Assets.*	1941 £ s. d.
£ s. d.				£ s. d.		
	To Reserve for Publications as per last Balance Sheet	1100 0 0		800 0 0	By Investments as per Schedule (cost or value when acquired)	2300 0 0
	Add Amount transferred from General Purposes Account	1800 0 0		500 0 0	„ Loan to General Purposes Account	2050 0 0
1100 0 0			2900 0 0	100 0 0	„ Sundry Debtor	
	„ Reserve for Library Books and Binding as per last Balance Sheet	250 16 0		50 16 0	„ Cash at Bank	74 19 3
250 16 0	*Add* Amount transferred from General Purposes Account	250 0 0		— — —	„ Cash on Deposit in Post Office Savings Bank	500 0 0
			500 16 0			
	„ Reserve for Research Fund, amount transferred from Research Fund :					
	On Deposit in Post Office Savings Bank	500 0 0				
	£900 2½% National War Bonds, 1949/51	900 0 0				
			1400 0 0			
100 0 0	„ Emile Mond Bequest as per last Balance Sheet...		100 0 0			
— — —	„ Excess of Income over Expenditure for year		24 3 3			
£1450 16 0			£4924 19 3	£1450 16 0		£4924 19 3

QUINQUENNIAL INDEX FUND.

£ s. d.		£ s. d.	£ s. d.		£ s. d.
— — —	To Cash receivable from Bureau of Chemical and Physiological Abstracts ...	50 0 0	— — —	By Sundry Debtor	50 0 0

The Chemical Society. Balance Sheets, 31st December, 1941.

PUBLICATIONS FUND.

1940	*Liabilities.*	1941		1940	*Assets.*	1941
£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.
9363 3 10	To Excess of Assets over Liabilities as per last Balance Sheet	9363 3 10		9363 3 10	By Investments as per Schedule (cost or value when acquired)	10,363 3 10
— — —	*Add* Amount received from Trustees of R. H. Parker—Legacy	1000 0 0				
			10,363 3 10			
£9363 3 10			£10,363 3 10	£9363 3 10		£10,363 3 10

RESEARCH FUND.

1940	*Liabilities.*		1941			1940	*Assets.*	1941
£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.		£ s. d.
	To Sundry Creditors		49 14 2			18,275 18 0	By Investments as per Schedule (cost or value when acquired)	18,377 9 5
	„ Excess of Assets over Liabilities as per last Balance Sheet			19,172 3 1		3 11	„ Sundry Debtors	15 0
17,044 1 0	*Add* Amount received from Trustees of W. S. Gilles—Balance of Legacy ...			101 11 5		700 0 0	„ Loan to General Purposes Account	
1,600 0 0	*Add* Excess of Income over Expenditure for year			680 13 7		245 15 4	„ Cash at Bank	254 16 10
528 2 1				19,954 8 1				
19,172 3 1	*Deduct* Amounts transferred to Special Reserve Fund:	£ s. d.						
	£900 2½% National War Bonds, 1949/51	900 0 0						
	Cash	500 0 0						
				1,400 0 0				
— — —			19,172 3 1		78 13 2			
			£19,221 17 3		£18,633 1 3	£19,221 17 3		£18,633 1 3

SPECIAL PUBLICATIONS FUND.

1940	*Liabilities.*		1941			1940	*Assets.*	1941
£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.		£ s. d.
	To Sundry Creditors		— — —			1600 0 0	By Investment as per Schedule (cost or value when acquired)	1600 0 0
	„ Excess of Assets over Liabilities as per last Balance Sheet			2301 3 11		1 10 5	„ Sundry Debtors	1 3 7
2209 4 5	*Add* Excess of Income over Expenditure for year			73 7 10		600 0 0	„ Loan to General Purposes Account	700 0 0
91 19 6						99 13 6	„ Cash at Bank	98 15 3
			2301 3 11					
			£2301 3 11		25 7 1			
					£2399 18 10	£2301 3 11		£2399 18 10

THE CHEMICAL SOCIETY. BALANCE SHEETS, 31ST DECEMBER, 1941.

SPECIAL LECTURES FUND.

1940 £ s. d.	1940 £ s. d.	*Liabilities.*	1941 £ s. d.	1941 £ s. d.
1114 18 9		To Excess of Assets over Liabilities as per last Balance Sheet	1159 10 7	
44 11 10		*Add* Excess of Income over Expenditure for year	— — —	
— — —		*Less* Excess of Expenditure over Income for year	5 8 6	
	1159 10 7			1154 2 1
	£1159 10 7			£1154 2 1

1940 £ s. d.	1940 £ s. d.	*Assets.*	1941 £ s. d.	1941 £ s. d.
1000 0 0		By Investment as per Schedule (cost or value when acquired)	1000 0 0	
100 0 0		„ Loan to General Purposes Account	— — —	
59 10 7		„ Cash at Bank	154 2 1	
	£1159 10 7			£1154 2 1

STAFF PENSIONS FUND.

£ s. d.	*Liabilities.*	£ s. d.	£ s. d.
907 14 0	To Excess of Assets over Liabilities as per last Balance Sheet	907 14 0	
— — —	*Add re* Superannuation	2166 17 9	
— — —	„ Excess of Income over Expenditure for year	100 0 0	
			3174 11 9
£907 14 0			£3174 11 9

£ s. d.	£ s. d.	*Assets.*	£ s. d.	£ s. d.
902 13 9		By Investments as per Schedule (cost or value when acquired)	3172 13 9	
5 0 3		„ Cash at Bank	1 18 0	
	£907 14 0			£3174 11 9

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

£ s. d.	£ s. d.	*Liabilities.*	£ s. d.	£ s. d.
1162 7 6		To Excess of Assets over Liabilities as per last Balance Sheet	1212 15 3	
50 7 9		*Add* Excess of Income over Expenditure for year	49 13 5	
	1213 15 3			1262 8 8
	£1213 15 3			£1262 8 8

£ s. d.	£ s. d.	*Assets.*	£ s. d.	£ s. d.
1101 7 11		By Investments as per Schedule (cost or value when acquired)	1101 7 11	
111 7 4		„ Cash at Bank	161 0 9	
	£1212 15 3			£1262 8 8

THE CHEMICAL SOCIETY. BALANCE SHEETS, 31ST DECEMBER, 1941.

CENTENARY FUND.

1940 £ s. d.	1940 £ s. d.	*Liabilities.*	1941 £ s. d.	1941 £ s. d.	1940 £ s. d.	1940 £ s. d.	*Assets.*	1941 £ s. d.
778 5 1		To Excess of Assets over Liabilities as per last Balance Sheet	1001 11 10		3 19 2		By Sundry Debtor	— — —
223 6 9		*Add* Excess of Income over Expenditure for year	25 1 11		6 16 4		„ Cash at Bank	10 15 6
	1001 11 10			1026 13 9	990 16 4		„ Cash on Deposit in Post Office Savings Bank and London Savings Bank	1015 18 3
	£1001 11 10			£1026 13 9		£1001 11 10		£1026 13 9

THE HERBERT SPENCER BEQUEST.

£ s. d.	£ s. d.		£ s. d.	£ s. d.	£ s. d.	£ s. d.		£ s. d.
257 7 6		To Balance unexpended at 31st December, 1940	24 9 6		4 2		By Sundry Debtor	— — —
		Less Excess of Expenditure over Income for			1 10 2		„ Cash at Bank	— — —
232 18 0		year	24 9 6		22 15 2		„ Cash on Deposit in Post Office Savings Bank and London Savings Bank	— — —
	24 9 6			— — —				
	£24 9 6			— — —		£24 9 6		— — —

THE FARADAY LECTURE FUND.

£ s. d.	£ s. d.		£ s. d.	£ s. d.	£ s. d.	£ s. d.		£ s. d.
380 13 1		To Excess of Assets over Liabilities as per last Balance Sheet	392 15 11		369 4 0		By Investment as per Schedule (cost or value when acquired)	369 4 0
		Add Excess of Income over Expenditure for			23 11 11		„ Cash at Bank	36 4 7
12 2 10		year	12 12 8					
	392 15 11			405 8 7				
	£392 15 11			£405 8 7		£392 15 11		£405 8 7

THE TILDEN LECTURE FUND.

£ s. d.	£ s. d.		£ s. d.	£ s. d.	£ s. d.	£ s. d.		£ s. d.
1678 18 7		To Excess of Assets over Liabilities as per last Balance Sheet	1916 9 3		1834 10 6		By Investments as per Schedule (cost or value when acquired)	1834 10 6
— — —		*Add* Balance of Legacy received from Executors	43 17 1		81 18 9		„ Cash at Bank	128 4 3
37 10 8		*Add* Excess of Income over Expenditure for year	2 8 5					
	1916 9 3			1962 14 9				
	£1916 9 3			£1962 14 9		£1916 9 3		£1962 14 9

SCHEDULE OF INVESTMENTS.

GENERAL PURPOSES.

Nominal Details.	*Cost or Value when Acquired.*	*Market Value 31st December, 1941.*
	£ s. d.	£ s. d.
£787 London, Midland and Scottish Railway 4% Debenture Stock	839 3 7	806 13 6
£1520 14*s.* 3*d.* Cardiff Corporation 3% Stock, 1914/54	1650 0 0	1505 10 1
£1400 India 2½% Stock	1316 1 0	1093 13 10
£2400 Bristol Corporation 2½% Debenture Stock, 1957	2070 2 0	2208 0 0
£2713 London, Midland and Scottish Railway 4% Preference Stock	3572 0 4	1831 5 6
£1200 Leeds Corporation 3% Stock	1143 1 0	1104 0 0
£1096 6*s.* 2*d.* Union of South Africa 3% Stock, 1954/64	1067 12 10	1096 6 2
£1200 London and North Eastern Railway 3% Debenture Stock ...	1033 11 0	912 0 0
£3629 6*s.* 9*d.* 5% Conversion Stock, 1944/64	3491 2 8	3838 0 6
£11,426 15*s.* 0*d.* 3½% Conversion Stock, 1961, or after	8874 2 2	12,226 13 4
£600 4% Funding Stock, 1960/90	480 0 0	687 0 0
£408 2*s.* 6*d.* 3% Funding Stock, 1959/69	394 11 5	412 4 1
	£25,931 8 0	£27,721 7 0

PUBLICATIONS FUND.

£5260 19*s.* 9*d.* 3½% Conversion Stock, 1961, or after	3645 12 8	5629 5 2
£3173 1*s.* 6*d.* 5% Conversion Stock, 1944/64	3199 18 7	3355 10 6
£817 P. & O. Steam Navigation Co. Deferred Stock	2060 0 0	1123 7 6
£603 London, Midland and Scottish Railway 4% Guaranteed Stock	457 12 7	587 18 6
£1000 3% Savings Bonds, 1955/65	1000 0 0	1000 0 0
	£10,363 3 10	£11,696 1 8

THE TILDEN LECTURE FUND.

£532 London Transport "B" 5% Stock	625 2 0	609 2 10
186 National Provincial Bank Shares £5 each, £1 paid "B" ...	678 18 0	599 17 0
£220 Metropolitan Water Board (Kent Water Works) 3% Deb. Stock	188 2 0	203 10 0
£376 3*s.* 5*d.* 3% Funding Stock, 1959/69	342 8 6	379 18 8
	£1834 10 6	£1792 8 6

SPECIAL RESERVE FUND.

£1000 3% National Defence Bonds	1000 0 0	1007 10 0
£400 2½% National War Bonds, 1946/48	400 0 0	400 0 0
£900 2½% National War Bonds, 1949/51	900 0 0	900 0 0
	£2300 0 0	£2307 10 0

RESEARCH FUND.

Nominal Details.	*Value or Cost when Acquired.*	*Market Value 31st December, 1941.*
	£ s. d.	£ s. d.
£1000 London and North Eastern Railway 4% 2nd Guaranteed Stock	1010 0 0	775 0 0
£1034 Great Western Railway 2½% Debentures	1049 15 11	703 2 5
£1122 Metropolitan Water Board 3% "B" Stock	1002 16 9	1088 6 10
£1483 London, Midland and Scottish Railway 4% Debenture Stock	1508 3 6	1520 1 6
£806 Victoria 3% Stock, 1929/49	706 6 2	777 15 10
£4498 11*s.* 0*d.* 5% Conversion Stock, 1944/64	4267 4 10	4757 4 4
£16,177 16*s.* 1*d.* 3½% Conversion Stock, 1961, or after	8833 2 3	10,890 5 1
	£18,377 9 5	£20,511 16 0

SPECIAL PUBLICATIONS FUND.

£2115 8*s.* 10*d.* 3½% Conversion Stock, 1961, or after	£1600 0 0	£2263 10

SPECIAL LECTURES FUND.

£1299 9*s.* 4*d.* 3½% Conversion Stock, 1961, or after	£1000 0	£1390 8 7

STAFF PENSIONS FUND.

£683 6*s.* 1*d.* 3½% Conversion Stock, 1961, or after	527 13 9	731 2 8
£371 17*s.* 1*d.* 5% Conversion Stock, 1944/64	375 0 0	393 4 9
£2100 2½% National War Bonds, 1946/48	2100 0 0	2100 0 0
£170 3% Savings Bonds, 1955/65	170 0 0	170 0 0
	£3172 13 9	£3394 7 5

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

£61 15*s.* 8*d.* 3½% Conversion Stock, 1961, or after	50 1 5	66 2 2
£1255 London, Midland and Scottish Railway 4% Debenture Stock	1051 6 6	1286 7 6
	£1101 7 11	£1352 9 8

THE FARADAY LECTURE FUND.

£374 19*s.* 0*d.* 3½% Conversion Stock, 1961, or after	£369 4 0	£401 3 11

F. P. DUNN, *Treasurer.*

We have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. We have also verified the Balances at the Bankers and the Investments. Certain figures relating to the Bureau of Chemical and Physiological Abstracts have not yet been subjected to audit by the Auditors of the Bureau and are therefore liable to adjustment.

224, REGENT STREET, W. 1.
27th February 1942.

W. B. KERN & Co.,
Chartered Accountants.

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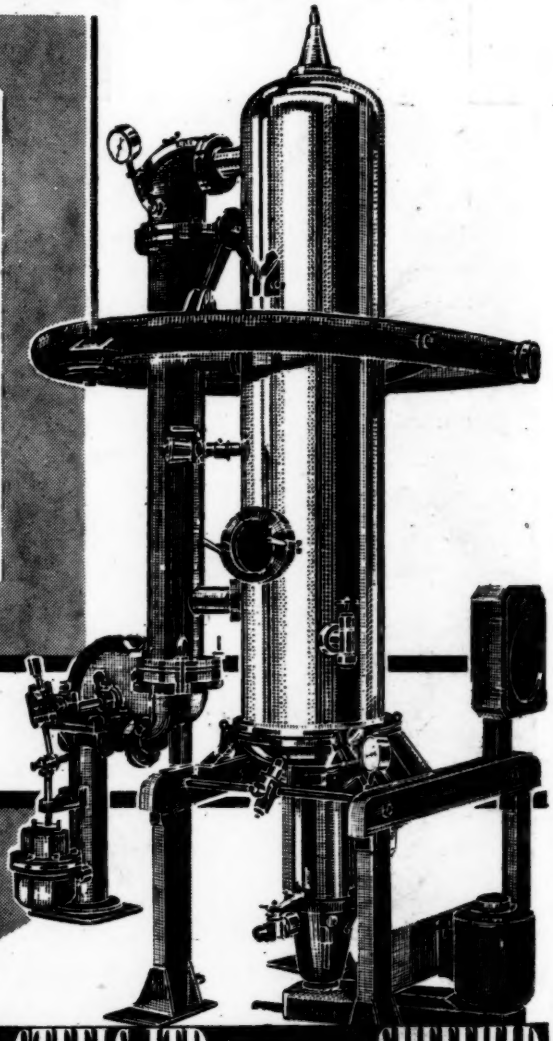

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